TECHNOLOGY QUARTERLY

AND

PROCEEDINGS OF THE SOCIETY OF ARTS.

VOL. XI. JUNE, 1898. NO. 2.

PROCEEDINGS OF THE SOCIETY OF ARTS.

THIRTY-SIXTH YEAR, 1897-98.

THURSDAY, January 13, 1898.

THE 505th regular meeting of the SOCIETY OF ARTS was called to order by the President at 8 P.M.

The records of the previous meeting were read and approved. Professor R. H. Richards read a paper[1] on the "Concentration of Ores, with Special Reference to Recent Investigations in this Subject." The separation of gold was the first process to be described. Next the concentration of lead, zinc, and copper ores was taken up, and the process of crushing, preliminary separating, sizing, and final separation were discussed at length. Turning to the theoretical principles involved in water sizing, Professor Richards described the difference in the proportions of ore and quartz at the various stages of free settling and of hindered settling. The relative advantages of these modes of settling for various kinds of ores were discussed, and principles used in determining the sieve scale and the best angle of slope for slime tables were explained.

After the speaker had received the thanks of the Society, the meeting was adjourned.

[1] Printed in full in *Technology Quarterly*, Vol. xi, No. 1, p. 54.

THURSDAY, January 27, 1898.

The 506th regular meeting of the SOCIETY OF ARTS was held this day at 8 P.M., Professor Swain in the chair.

The records of the previous meeting were read and approved. Mr. B. C. Batcheller, of Philadelphia, was introduced and read a paper on "A New System of Pneumatic Dispatch Tubes." He said that the history of pneumatic transit began practically in London in 1853, when the Electric and International Telegraph Company constructed the first tube for dispatching their telegrams. This tube was one and a half inches in diameter, and two hundred and twenty-five yards in length. Later longer tubes were constructed in London, Paris, Berlin, and Vienna.

The history of large pneumatic tubes for the transportation of mail began in Philadelphia in the winter of 1892–93. The system used in Philadelphia was described in detail, and also the methods employed in manufacturing the tubes. The straight pipes are of cast-iron similar to water pipes, and bored to a uniform diameter. The bends are made of brass tubing. Transmitters are provided with a time-lock to prevent collisions. Open receivers are used at far ends of the tubes, while in a loop a closed receiver is employed. This is provided with a circular plate to prevent the escape of air. The construction of stations, switches, electric block system, and carriers were described. The method of laying the pipes was discussed and then the Boston system, which was opened on the 17th of December, was discussed in detail. The speaker then turned to the theory of pneumatic transit, and exhibited curves showing the decrease of pressure with an increase of velocity as the carrier moves along the tube. In conclusion he gave an account of the ingenious method employed to determine the position of an obstruction in the tube. The calculation is made from observations of the time between a pistol shot and its echo. The paper was illustrated by the lantern, and specimens of carriers were exhibited. During the discussion which followed Mr. Batcheller said that the speed increases with the diameter of the tube.

It was voted to thank the speaker for the great pains he had taken to explain and illustrate the subject, and the Society then adjourned.

THURSDAY, February 10, 1898.

The 507th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Mr. N. M. Lowe in the chair.

The record of the previous meeting was read and approved. Messrs. Edward D. Densmore, of Boston, Will J. Sando, of Boston, and Rufus F. Herrick, of Rockaway, New York, were duly elected Associate Members of the Society.

Dr. Leonard Waldo, of Bridgeport, Connecticut, was introduced and read a paper on the "History and Present Development of the American Bicycle." He said that the first great advance in the manufacture of bicycles came with the introduction of machines of precision for the manufacture of interchangeable parts, and by the invention of pneumatic tires it became possible to use hard bearings with rolling balls. He spoke of the great care used in selecting the materials, all of which are forged and drawn cold, and he described in detail the various tests employed to determine the strength of materials and the efficiency of the machine.

Three difficulties were met with in the attempt to construct a chainless wheel with bevelled gear: (1) To find material for the tubular shaft that would resist torsion; (2) to invent machines that would cut tooth gears rapidly; (3) to harden without deformation. These have all been overcome. The paper was illustrated by lantern slides and a model of tooth gear. A discussion followed the reading of the paper. It was voted to thank Dr. Waldo for his interesting paper, and the Society adjourned.

THURSDAY, February 24, 1898.

The 508th meeting of the SOCIETY OF ARTS was held at the Institute at 8 P.M., Mr. Desmond FitzGerald in the chair.

The record of the previous meeting was read and approved.

Mr. Fred B. Forbes, of Somerville, was duly elected an Associate Member of the Society. The following papers were presented by title: "Best Resistance for a Sensitive Galvanometer," by F. A. Laws; "Investigation of the Theory of the Solubility Effect in the Case of Tri-ionic Salts," by A. A. Noyes and E. H. Woodworth.

Mr. Henry B. Wood, Engineer of the State Survey, was then introduced and read a paper on "State, Town, and City Boundaries."

He gave the history of the attempts to determine the boundaries of Massachusetts, and described the present condition of the boundary lines. This was followed by a detailed account of the recent work of the Topographical Survey in determining the boundary lines between this State and New York and Rhode Island. In the work on the New York boundary the heleotrope was employed to obtain long lines of sight, one of these lines being forty-one miles in length. It was possible by this means to determine intermediate points to within five-eighths of an inch.

Mention was made also of the delineation of town boundaries; 2,500 corners have been located, and the work is less than half finished. In conclusion it was shown how the triangulation of the State is related to the determination of boundaries. The paper was illustrated by a large number of lantern views. A discussion followed, after which the Society adjourned.

THURSDAY, March 10, 1898.

The 509th meeting of the SOCIETY OF ARTS was called to order this day at 8 P.M., Mr. Blodgett in the chair.

The record of the previous meeting was read and approved.

Mr. A. T. Hopkins then read a paper, prepared by Mrs. Ellen H. Richards and himself, on "Certain Sanitary Aspects of Jamaica." He began with a general description of the country, and then gave an account of a journey which he made around the island for the purpose of collecting samples from the water supplies. The results of analyses made by Mrs. Richards were shown on a chart. It was found that distance from the sea, the presence of mountains, and the amount of rainfall and evaporation had marked influence upon the normal distribution of chlorine. The present methods of obtaining water and of disposing of sewage were described, and also a sewerage plant installed by Mr. Hopkins at Port Antonio. He concluded with an account of the recent epidemic of yellow fever, which he had traced to its source in two sailors recently from a Cuban port, who became sick in Kingston soon after their arrival. From them the disease spread after the usual manner of infectious diseases. The paper was illustrated.

During the discussion which followed Professor Sedgwick spoke of the importance of construction of a normal chlorine chart as a basis for

the detection of injurious substances in water supplies, and complimented Mr. Hopkins upon his success in tracing the yellow fever epidemic.

After a vote of thanks to the speaker, the Society adjourned.

THURSDAY, March 24, 1898.

The 510th meeting of the SOCIETY OF ARTS was held in Room 22 of the Walker Building at 8 P.M., with Mr. Blodgett in the chair.

The record of the previous meeting was read and approved.

The Chairman introduced Mr. E. M. Smiles, of New York, who exhibited an apparatus for the production of X-rays.

A short discussion followed the exhibition, after which the Society adjourned.

THE CONSTITUTION OF STEEL CONSIDERED AS AN ALLOY OF IRON AND CARBON.

By ALBERT SAUVEUR.

Read April 28, 1898.

It has been conclusively established that in unhardened steel, at least, the totality of the carbon is combined with a portion of the iron forming the carbide Fe_3C, which is then distributed throughout the balance of the iron.[1] Steel may therefore be considered as a mixture or an alloy of iron and the carbide Fe_3C, and I shall endeavor to show that if we look upon steel in this light, the formation of its structure follows very closely the laws which govern the formation of the structure of a certain class of binary metallic alloys, namely, that group of alloys whose component metals form neither definite compounds nor isomorphous mixtures.

Great advance has been made in recent years in our knowledge of the true constitution of metallic alloys. Much activity was created in this field of research through the work of special committees organized in England by the Institution of Mechanical Engineers, and in France by the Société d'Encouragement pour l'Industrie Nationale. Among those investigators whose work has been most fruitful, the names of Dr. Guthrie, Roberts-Austen, H. Le Chatelier, Heycock and Neville, Charpy, Gautier and Behrens stand preeminent.

The study of the structure of alloys and of industrial metals has even called into existence a new department of science, for the microscope has revealed to us that all alloys and all industrial metals, which always contain a certain amount of impurities, are made up of constituents which may be regarded as minerals, for they possess all the characteristics of true minerals; and as the study of rocks created the science of petrography, so from the study of the constitution of metals

[1] I purposely ignore here the small amount of graphitic carbon often found in high carbon steel after annealing.

and alloys was developed a new department of metallurgy, called metallography.

One of the most brilliant achievements of these recent investigations is to be found in the discovery that the structure of metallic alloys is controlled by the same laws which had been known for some time, to regulate the constitution of mixtures of melted salts and of frozen saline solutions. In other words, the greatest analogy exists between the structure of solid saline solutions and that of metallic alloys. The latter must be considered as true solutions. The fact that they are solid at the ordinary temperature, while saline solutions are liquid, has alone prevented the identity of the laws which govern the formation of the structure of both classes of substances, when they assume the solid state, from being discovered at a much earlier date. With a view of offering a rationale for the constitution of steel I shall briefly recall the working of these laws, although time permits me to do so only in their broadest outline.

Saline Solutions. — We all know that by dissolving common salt, sodium chloride, in water, we lower the freezing point of the water. By increasing the amount of salt the freezing point of the resulting mixture is, at first, correspondingly lowered, until it contains a certain percentage of salt. The lowest possible freezing point of a solution of sodium chloride in water is then reached, and further addition of salt will gradually raise the freezing point of the brine.

Dr. Guthrie found that the mixture which has the lowest possible freezing point contains about 23.50 per cent. of NaCl; and as the hydrate containing 10 molecules of water would require 24.50 per cent. of salt, Dr. Guthrie inferred that the solution of lowest freezing point was an hydrate of the formula $NaCl + 10\ H_2O$. He proposed for it and for all similar mixtures, *i. e.*, for all saline solutions of lowest freezing points, the name of *cryohydrate*, by which he meant to imply that they can only exist in the solid state, at a low temperature.

Figure 1 shows the curve of solubility, or the freezing curve, which is evidently the same thing, of a solution of sodium chloride in water. The abscisses represent the composition, the ordinates the temperatures at which the various mixtures freeze. The curve is made up of two branches which meet at a point E corresponding to a temperature of $-22°$ C, and to a solution containing 23.50 per cent. of NaCl, *i. e.*, to the composition and freezing point of the cryohydrate.

Supposing the mixture placed in a proper cooling medium, let us see what happens when a solution poorer in salt than the cryohydrate reaches its freezing point. It is at that instant saturated with water and further cooling will cause the *formation of ice.* If a thermometer be placed in the solution it will then indicate a retardation in the rate of cooling which, of course, denotes an evolution of latent heat and marks the beginning of solidification. If the corresponding temperature be plotted on the diagram it will give one point of the branch *M E.* The formation of pure ice causes the remaining liquid to become richer in salt, and as its freezing point is thereby correspondingly lowered, the deposition of ice does not take place at a constant temperature, but proceeds as the temperature is further lowered. The portion remaining liquid meanwhile becomes richer and richer in salt, until at a temperature of — 22° C it reaches the composition of the cryohydrate. The remaining liquid then solidifies *as a whole and at a constant temperature;* the thermometer placed in the mixture remains stationary until the whole mass has solidified. The heat which is here evolved is the latent heat of solidification of the cryohydrate, and if the corresponding temperature be plotted on the diagram it will give one point of the horizontal line. If the application of cold be continued after the whole mass is solid, the fall of temperature resumes again its normal rate.

A frozen saline solution, then, containing less salt than the cryohydrate, will be made up of crystals of ice surrounded by the frozen cryohydrate. If the solution contains more salt than the proportion found in the cryohydrate, when a certain temperature is reached, the thermometer indicates an evolution of heat which marks the beginning of solidification and corresponds to the formation of *crystals of salt* (sometimes hydrated), for the solution is at that temperature saturated with salt, and further cooling must cause the deposition of salt. The crystals of salt increase in quantity as the temperature continues to fall. The remaining liquid meanwhile becomes correspondingly poorer in salt, approaching more and more the composition of the cryohydrate which it reaches at a temperature of — 22° C. At that instant the portion remaining liquid solidifies as a whole and at a constant temperature, as indicated by the thermometer, which at this stage remains stationary until the entire mass has solidified. The plotting of the corresponding temperature gives another point of the horizontal line. The frozen mass is then made up of crystals of salt

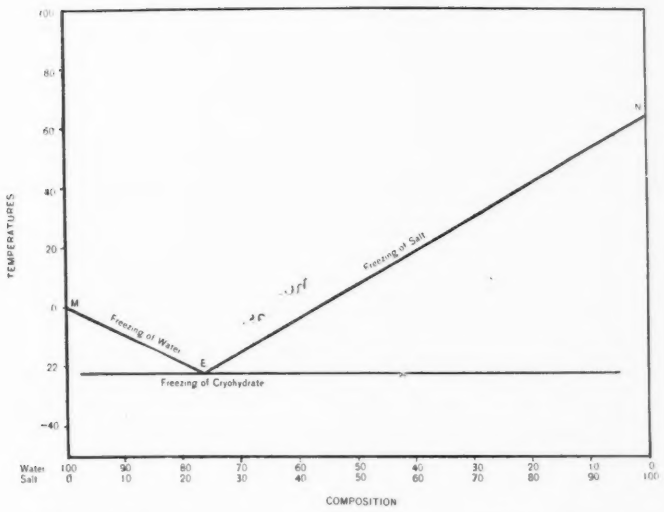

FIG. 1. — CURVE OF SOLUBILITY OF AQUEOUS SOLUTIONS OF NaCl.

(See pages 79–80.)

surrounded by the solid cryohydrate. If the solution has a composition identical to that of the cryohydrate, it will not freeze until it has reached a temperature of — 22° C, when it will solidify as a whole and at a constant temperature.

The composition of the cryohydrate, it is seen, is independent of the composition of the solution, but the proportions of cryohydrate and of ice or of cryohydrate and of salt found in the frozen solution, depend, of course, upon the amount of salt in the solution. The branches *M E* and *N E* correspond, therefore, to the *beginning* of the evolutions of heat which accompany the beginning of solidification of ice or of salt. Hence they also represent the solubility of salt in water at various temperatures. The horizontal line corresponds to the evolutions of heat corresponding to the solidification of the cryohydrate, and indicates that such solidification takes place at a constant temperature, which is the same whatever the composition of the original solution.

While saline solutions, therefore, containing various proportions of salt *begin* to freeze at temperatures which depend upon their degree of concentration, they all *finish* freezing at the same temperature, namely, at — 22° C, the freezing point of the cryohydrate.

Seeing that one branch of the curve represents the formation of crystals of ice in brines poorer in salt than the cryohydrate, while the other branch corresponds to the formation of crystals of salt in solutions richer in salt, the conclusion is almost irresistible that their meeting point must correspond to a *simultaneous deposition of ice and salt,* and that the frozen cryohydrate, therefore, must be a mechanical mixture of ice and salt, probably in an extremely minute state of division, which would outwardly give it the appearance of a definite compound; and indeed, Mr. Offer has shown that the cryohydrates do not form distinct and transparent crystals, but opaque masses, and that alcohol dissolves the ice and leaves a crystalline network of solid salt; also that their heat of dissolution is equal to the sum of the heats of dissolution of the ice and of the salt; finally, that the specific gravity is equal to the mean of those of both constituents, which facts argue strongly in favor of the cryohydrates being merely mechanical mixtures of ice and salt.

Mr. Ponsot, moreover, using colored salts, has ascertained that the cryohydrates were actually made up by the juxtaposition of crystals of pure ice and of salt, the salt being sometimes hydrated. We shall

presently find some further evidences that the cryohydrates are merely mechanical mixtures of this description.

What has been said regarding brines applies to all aqueous saline solutions; they all give rise upon cooling to the formation of cryohydrates, *i. e.*, of solutions having a definite composition, and which freeze at a constant temperature which is also the lowest possible in each series.

If we now pass to mixtures of melted salts which form neither definite compounds nor isomorphous mixtures, we find that upon solidifying, the formation of their structure is regulated by exactly the same laws. They, too, form a mixture of definite composition and lowest melting point which solidifies at a constant temperature. Whichever salt is present in excess solidifies first until the composition of the molten mass has reached that of the mixture of lowest melting point. In these cases the water is simply replaced by another salt; and if we consider water as fused ice, we need not make any distinction between these two classes of substances, namely, between aqueous saline solutions and mixtures of melted salts.

If I have dwelt at such length upon the constitution of frozen saline solutions, it is because it will help us to account for the structure of metallic alloys.

Metallic Alloys. — The present theory of the constitution of alloys so brilliantly worked out classifies all such mixtures into three classes:

I. Alloys which give neither definite compounds nor isomorphous mixtures.

II. Alloys which form definite compounds.

III. Alloys which form isomorphous mixtures.

For our purpose we need only consider the first group, namely, those alloys which form neither definite compounds nor isomorphous mixtures — and to make the matter clearer, let us take an individual instance, that of silver and copper alloys.

Figure 2 shows what is known as the curve of fusibility of silver and copper alloys. The abscisses represent the composition of the alloys; the ordinates the temperatures at which they solidify. Attention need not be called to the striking resemblance between this curve and that of the saline solution just examined. The former was called a curve of solubility, but solubility and fusibility represent here, obviously, the same phenomenon. Both are freezing curves. Fusibility applies to mixtures solid at the ordinary temperature; solubility to those liquid at that temperature.

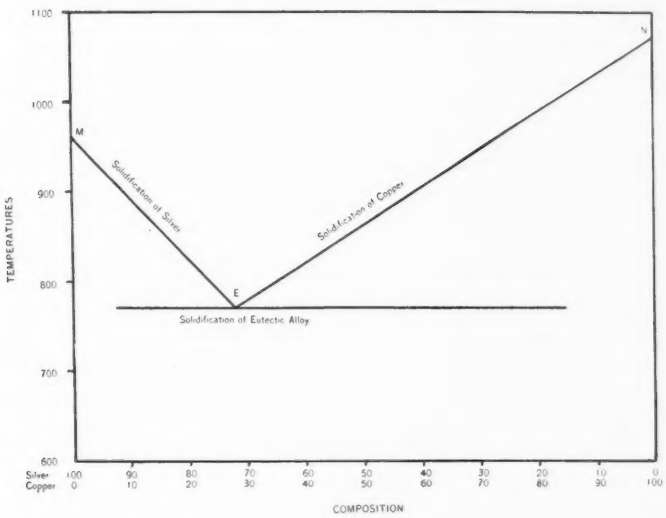

FIG. 2. — CURVE OF FUSIBILITY OF SILVER AND COPPER ALLOYS.

(See pages 82-83.)

Like the curve of solubility of saline solutions, the curve of fusibility of metallic alloys is obtained by cooling from the molten state mixtures containing various proportions of the two component metals, and by carefully ascertaining, most conveniently by means of a Le Chatelier pyrometer, the temperature at which the cooling is momentarily arrested, or its rate retarded, which indicates an evolution of latent heat and marks the beginning of the solidification of the alloys. As in the case of saline solutions all alloys of silver and copper, with one exception, exhibit a second evolution of heat occurring always at the same temperature and corresponding, therefore, to an horizontal line in the diagram.

The curve is composed of two branches starting respectively from the melting points of pure silver and of pure copper, and meeting at a temperature of 770° C, and for a composition corresponding to 28 per cent. of copper and 72 per cent. of silver. The mixture of that composition has the lowest possible melting or freezing point of all silver and copper alloys. It is called the *eutectic alloy*, a name proposed for it and for all similar alloys, by Dr. Guthrie. It is seen at once that the greatest analogy exists between the eutectic mixtures of metallic alloys and the cryohydrates of saline solutions.

There are two cases to be considered. The composition of the alloy may correspond exactly to that of the eutectic alloy or it may differ from it. In the first case, as the mixture cools from a high temperature, it remains liquid until it reaches the solidification point of the eutectic alloy, 770° C, when it solidifies as a whole, and at a *constant temperature* as indicated by the pyrometer, which at this stage remains stationary until the whole mass has solidified. Such a mixture behaves exactly like a saline solution having a composition identical to that of the cryohydrate; the solid mass is made up entirely of the eutectic alloy. See Plate I,[1] Figure 1.

If the composition of the alloy differs from that of the eutectic mixture, *i. e.*, if one of the constituents is present in excess with regard to that composition, the silver for instance, then when the cooling mass reaches a certain temperature the silver in excess begins to solidify exactly as did the water in the case of a saline solution. This deposition is accompanied by an evolution of heat indicated by the

[1] The figures of this plate, with the exceptions of Figures 4 and 6, are reproductions from photo-micrographs taken by Mr. Osmond. The Metallographist, Vol. I, No. 1, January, 1898.

pyrometer, and which, when the corresponding temperature is plotted, gives one point of the branch *M E*. The separation of pure silver continues until the portion remaining liquid, and which becomes all the while poorer in silver, has reached the composition of the eutectic alloy, 72% Ag + 28% Cu. At that instant the silver is saturated with copper, the copper is saturated with silver, and both metals solidify together at a constant temperature.

Alloys containing a larger percentage of silver than the eutectic mixture will, therefore, be made up of crystalline particles of silver in a matrix of the eutectic alloy. Plate I, Figure 2, exhibits the structure of an alloy containing 85 per cent. of silver. The large black areas represent the pure silver; the composite constituent forming the network is the eutectic alloy. The preparation was heated to a purple color, which accounts for the dark appearance of the silver.

If it be the copper which is present in excess with regard to the composition of the eutectic alloy, it is pure copper which begins to solidify when a certain temperature is reached. The solidification of copper continues until the portion remaining liquid has reached a composition identical to that of the eutectic alloy; it then solidifies as a whole and at a constant temperature, which when plotted gives one point of the horizontal line.

Alloys of silver and copper containing a larger proportion of copper, therefore, than the eutectic mixture, will be made up of crystalline particles of copper surrounded by the eutectic alloy. This is well shown in Figure 3, Plate I, which represents the structure of an alloy containing 65 per cent. of copper, *i. e.*, a large excess of that metal. The large white areas represent the pure copper; the constituent made up of grains or plates alternately light and dark is the eutectic alloy.

What, then, is the nature of these eutectic alloys? Seeing that they always had a definite composition, whatever the composition of the original alloy, and also on account of the closeness of their fractures, which often have a conchoïdal appearance, it was thought for many years that they were definite compounds, although their compositions seldom correspond to exact simple ratio of the atomic weights of the components.

On the other hand, seeing that one branch of the curve of fusibility corresponds to the solidification of pure copper, the other to the solidification of pure silver, it would seem highly probable that their

FIG. 1. — ALLOY OF SILVER AND COPPER.
Cu, 28 per cent.; Ag, 72 per cent.
Magnified 600 diameters.

FIG. 2. — ALLOY OF SILVER AND COPPER.
Cu, 15 per cent.; Ag, 85 per cent.
Magnified 600 diameters.

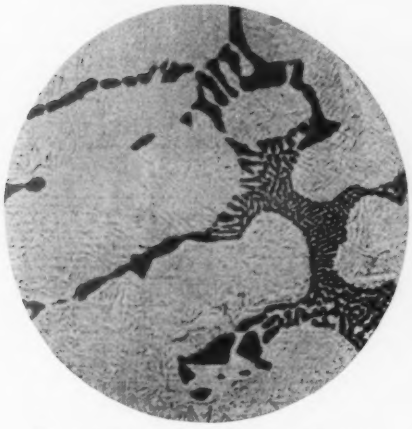

FIG. 3. — ALLOY OF SILVER AND COPPER.
Cu, 65 per cent.; Ag, 35 per cent.
Magnified 600 diameters.

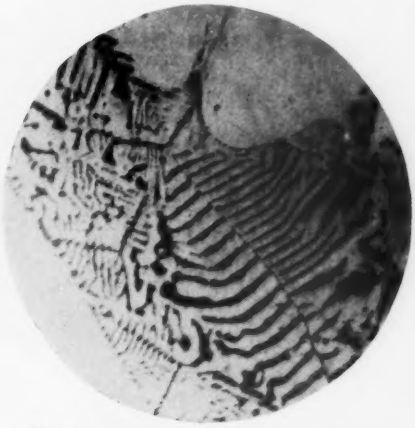

FIG. 4. — ALLOY OF SILVER AND ANTIMONY.
Ag, 66 per cent.; Sb, 34 per cent.
Magnified 500 diameters.

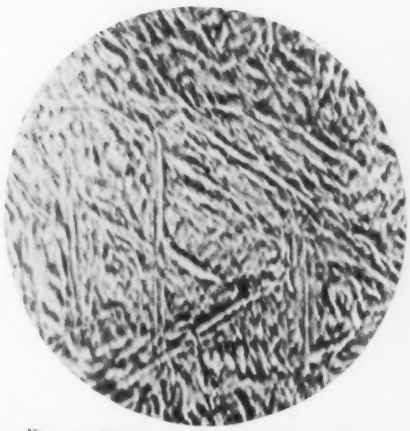

FIG. 5. — STEEL — 0.45 PER CENT. CARBON.
Hardened.
Magnified 1,000 diameters.

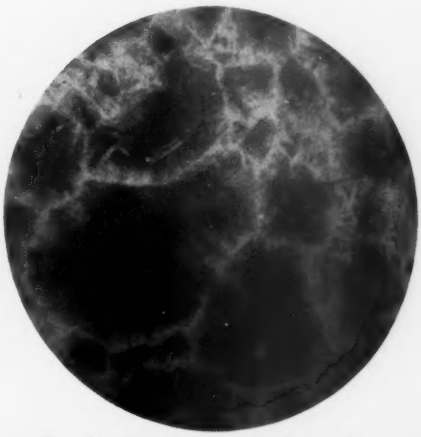

FIG. 6. — STEEL — 0.09 PER CENT. CARBON.
Hardened.
Magnified 250 diameters.

meeting point must correspond to the simultaneous solidification of silver and copper, and that the eutectic alloy is merely a mechanical mixture of the two constituents. The microscope has shown that such, indeed, is the case. All eutectic alloys are made up of extremely minute crystals or plates of the two components in close juxtaposition. This is well illustrated in Figure 1, Plate I, which shows the structure of the eutectic alloy of silver and copper under a magnification of 600 diameters. Figure 4, Plate I, reproduced from a photomicrograph of Mr. Charpy, presents another beautiful instance of the characteristic structure of eutectic mixtures. The component metals are here silver and antimony, and the alloy contains an excess of silver which is represented in the photograph by light areas.[1]

In the fact that eutectic alloys are mechanical mixtures, we find an additional important evidence that such must also be the constitution of cryohydrates, whose formation is so similar to that of eutectic alloys.

On account of the minuteness of their constituents, eutectic mixtures often require very high power for their resolution, and they frequently present under the microscope a beautiful play of interference colors, strongly suggestive of mother-of-pearl.

Alloys of Iron and Fe_3C. — With the laws which control the formation of the structure of alloys fresh in our minds, we shall have no difficulty in accounting for the structure of steel as revealed to us by the microscope. In Figure 3 the abscisses represent the composition of the metal in terms of iron and the carbide Fe_3C, the corresponding percentages of carbon being indicated between brackets. The ordinates represent the temperatures at which some evolutions of heat occur during the undisturbed cooling of the metal.

By allowing samples of steel containing various amounts of carbon to cool from a high temperature, and carefully observing the rate of cooling by means of a Le Chatelier pyrometer, when a certain temperature is reached, which varies with the carbon content, a sudden retardation occurs which denotes, of course, some evolution of heat. By plotting the corresponding temperatures, the curve *M E N* is obtained. The diagram also indicates that on further cooling a second evolution of heat occurs, this time at nearly the same temperature, whatever the degree of carburization of the metal. Graphically,

[1] This sample was treated with sulphuretted hydrogen, which blackens the silver while it has no action upon the antimony. The reproduction, however, was prepared from a negative print, so that the silver here appears white instead of dark.

therefore, it is represented by a nearly horizontal line.[1] This second evolution of heat is generally very marked. It is sometimes so intense as to produce an actual rise in the sensible temperature of the steel, a "recalescence" of the cooling metal. It is why the phenomenon is known by the name of recalescence, and the temperature at which it occurs called the temperature or the point of recalescence. It is a critical temperature of vital importance; in passing through it the structure of the steel is entirely changed, and nearly all its properties, chemical, physical, and mechanical, markedly altered.

The appearance of the diagram obtained in this way recalls at once the curve of solubility of saline solutions and that of fusibility of metallic alloys. Here again we have two branches of curves, meeting in this case at a temperature of about 670° C., and for a composition corresponding to 12 per cent. of Fe_3C (or 0.8 per cent. carbon) in the steel. We have also a nearly horizontal line passing by the point of intersection. The analogy between the three curves (Figures 1, 2, and 3) is, indeed, so striking that it will readily suggest, I believe, the inference that the branch *M E* (Figure 3) corresponds to the separation or segregation (we cannot use the word solidification here, for at this temperature the whole mass is solid) of the iron, and the branch *N E* to the segregation of the carbide Fe_3C, while the point *E* marks

[1] The temperatures at which retardations occur during the cooling of steel do not, of course, when plotted, give absolutely straight lines; experimental errors alone would preclude such possibility. Moreover, slight amounts of impurities have a notable influence upon the position of the retardation, and it is quite impossible to obtain various grades of steel absolutely free from impurities or containing exactly the same amount. It is sufficient for our reasoning that the curve should be made up, as it is, of two branches which meet in the region indicated. The two branches appear not to deviate very much from straight lines, and might possibly coincide exactly with them if experimental errors and other disturbing factors could be eliminated. It should also be stated that these evolutions of heat do not begin and end at the same temperature, but, on the contrary, cover a noticeable range — sometimes as much as 50° C. or more — so that the first and second evolutions run together long before a carbon content of 0.8 per cent. has been reached, with the result that steel containing over 0.50 per cent. carbon appears to have only one retardation extending over a considerable range of temperature: the end of the first retardation merges into the beginning of the second.

Finally, when the metal contains less than about 0.25 per cent. carbon, a third retardation is detected, located between the first evolution and the point of recalescence. It has been purposely left out of this diagram because it would have rendered the resemblance which the latter bears to the curve of solubility or of fusibility just examined, less marked, and to little purpose, for the existence of a third evolution of heat confined to these narrow limits does not sensibly affect the strength of the deduction drawn from the striking analogy of the curves.

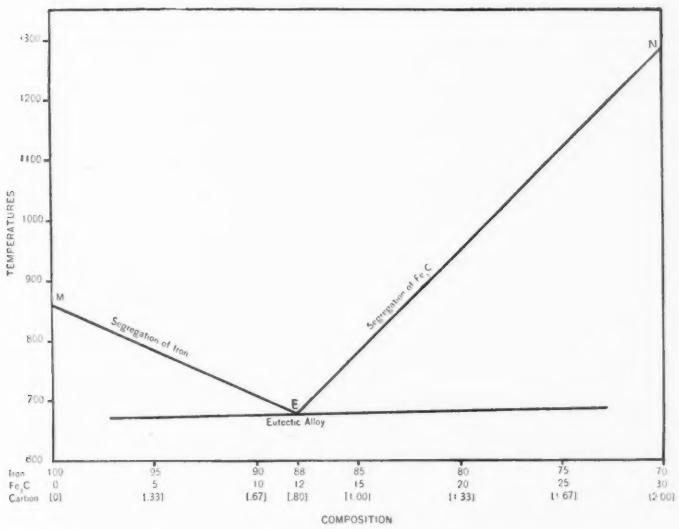

FIG. 3. — CURVE INDICATING EVOLUTIONS OF HEAT (ACCOMPANIED BY STRUCTURAL CHANGES) OCCURRING DURING THE COOLING OF STEEL.

(See pages 85–86.)

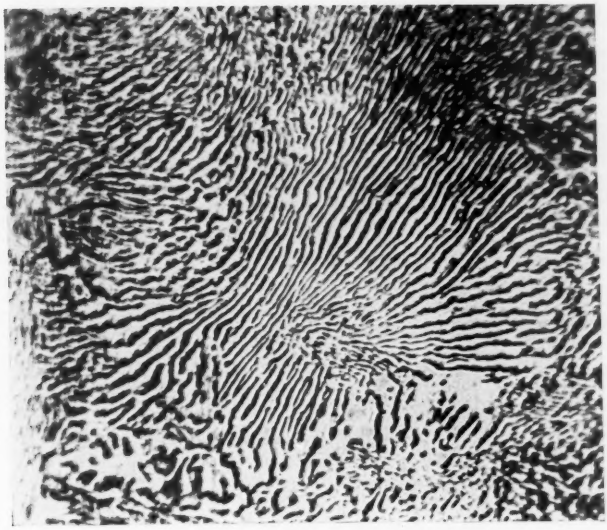

FIG. 1. — STEEL — 1 PER CENT. CARBON.
Magnified 1,000 diameters.

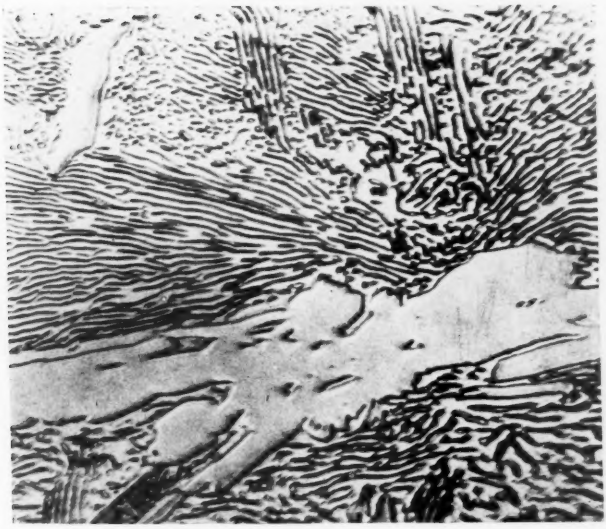

FIG. 2. — STEEL — 1.5 PER CENT. CARBON.
Magnified 1,000 diameters.

FIG. 1. — STEEL — 0.45 PER CENT. CARBON.
Magnified 1,000 diameters.

FIG. 2. — STEEL — 1.5 PER CENT. CARBON.
Quenched at 1050° C. in ice water.
Magnified 1,000 diameters.

the formation of a eutectic alloy of iron and Fe_3C, *i. e.*, a mechanical mixture whose structure should be made up of small crystalline plates or grains alternately of iron and Fe_3C, and resulting from the simultaneous segregation of the two constituents. If we are right, steel containing less than 12 per cent. of Fe_3C (0.8 per cent. carbon) should be made up of crystalline grains of pure iron (at least of carbonless iron) surrounded by the eutectic alloy of Fe and Fe_3C; steel more highly carbonized should be formed of grains of the carbide Fe_3C surrounded by the eutectic alloy, while if the metal contains exactly 0.8 per cent. carbon it should be entirely made up of the eutectic alloy.

Such conclusions are confirmed in every particular by the microscopical examination of the structure of various grades of steel. Plate II, Figures 1, 2, and Plate III, Figure 1, show the reproduction of some beautiful photomicrographs taken by Mr. Osmond under a magnification of 1,000 diameters.[1] Figure 1 exhibits the structure of the eutectic alloy of Fe and Fe_3C. It presents all the structural characteristics of eutectic mixtures, being made up of thin plates alternately of Fe and Fe_3C. These plates seldom exceed $\frac{1}{40,000}$ of an inch in thickness; the plates of iron are somewhat darkened (or rather deprived of their metallic luster) by the polishing and etching, while the plates of Fe_3C are left white and brilliant, and stand slightly in relief. The arrangement is, therefore, similar to that of the reflection gratings of physicists, and explains the pearly appearance of this remarkable constituent.

The steel of Figure 2, Plate II, contains 1.50 per cent. of carbon, therefore an excess of Fe_3C with regard to the composition of the eutectic alloy. The white portion standing in relief represents areas of Fe_3C. It is surrounded by the eutectic alloy. Figure 1, Plate III, shows the structure of a steel containing less carbon, and therefore more iron, than the eutectic mixture. The light background indicates the excess of iron. The accuracy of the deduction drawn from the appearance of the curve of Figure 3 is further illustrated by the lowest row of drawings of Plate IV, which show the structure of a series of slowly cooled steels of ascending carbon content. They were drawn directly from the microscope under an original magnification of 250 reduced in the reproduction to 72. The shaded constituent represents the eutectic alloy; the pure iron has been left white, which is its appearance under the microscope; while the carbide Fe_3C is here rep-

[1] The Metallographist, Vol. I, No. 1, January, 1898.

resented by black areas to distinguish it more readily from the iron, although in reality it has a brilliant, metallic appearance.

Mineralogical names have been given to these constituents: Pure iron has been called *ferrite*. The carbide Fe_3C, *cementite*, because abundant in cement steel, while the name of *pearlyte* has been given to the eutectic alloy of Fe and Fe_3C, *i. e.*, of ferrite and cementite, because of its pearly appearance.[1] The composition of pearlyte, like that of any eutectic alloy, remains the same, whatever the composition of the steel, *i. e.*, whatever its carbon content. It always contains in the neighborhood of 0.8 per cent. of carbon.[2] The relative proportions of ferrite and pearlyte, however, or of cementite and pearlyte in the steel, vary, of course, according to the degree of carbonization.

Very low carbon steels, then, are made up of a matrix of iron or ferrite, with here and there a particle of pearlyte (Plate IV, Figure 4); the fine black lines indicate the junction lines between the grains of ferrite. As the carbon increases the amount of pearlyte increases proportionally (Figures 7 and 10), until with 0.8 per cent. of carbon the metal is made up entirely of pearlyte (Figure 12). It is then said to be saturated. With further increase of carbon, cementite makes its appearance, increasing in quantity with the carbon content, causing, of course, a corresponding decrease in the amount of pearlyte (Figures 14 and 16).

The structural composition of any carbon steel may readily be calculated from its carbon content. If the steel contains less than 0.8 per cent. of carbon it is made up of ferrite and pearlyte. Let x be the percentage of ferrite, y that of pearlyte; we have

$$(1) \quad x + y = 100;$$

and since the totality of the carbon is found in the pearlyte and forms 0.8 per cent. of its composition, we have the second equation:

$$(2) \quad \frac{0.8}{100}\, y = C,$$

in which C represents the known amount of carbon in the steel.

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[1] These very appropriate names were suggested by Professor Henry M. Howe, and have been quite universally adopted.

[2] Professor Arnold experimenting with exceptionally pure carbon steels, especially prepared, finds that pearlyte contains nearly 0.9 per cent. carbon. In the case of commercial steel, however, the carbon content of pearlyte is nearer 0.8 per cent. Impurities, and it would seem manganese especially, have a tendency to lower the percentage of carbon in pearlyte.

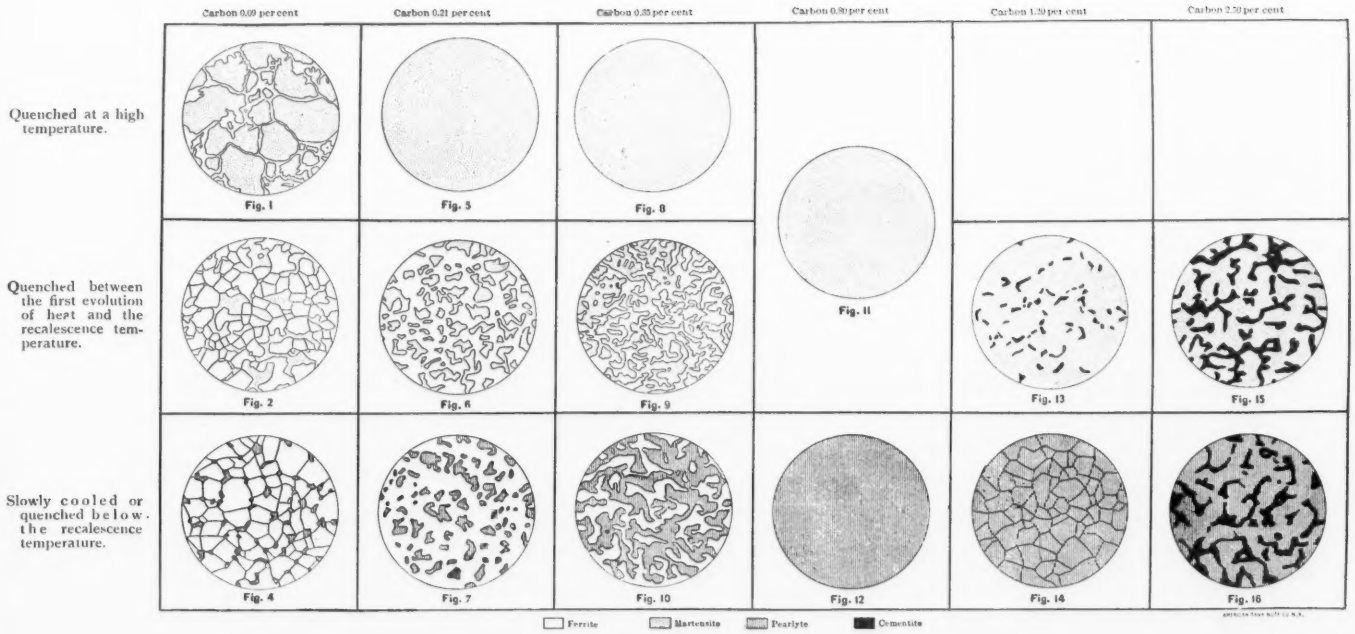

PLATE IV. — MICROSTRUCTURE OF STEEL.

Magnified 72 diameters. (Reduced from original magnification of 250.)

If the metal contains more than 0.8 per cent. carbon, it is composed of pearlyte and cementite. If z be the percentage of cementite, we have

$$(1) \quad y + z = 100.$$

Pearlyte contains 0.8 per cent. *C*, and cementite 6.67 per cent. *C* (which is the proportion required by the formula Fe_3C), and since the sum of the pearlyte carbon and of the cementite carbon must be equal to the total carbon in the steel, we have the second equation:

$$(2) \quad \frac{0.8}{100} y + \frac{6.67}{100} z = C.$$

While the similarity between the formation of the structure of alloys or of frozen saline solutions and that of carbon steel is indeed striking, there is one feature in which the two phenomena differ, which is momentous. In the case of alloys or of saline solutions the curves of fusibility or of solubility, which indicate the temperature at which the constituent present in excess begins to segregate from the mass, also represent the beginning of the *solidification* of that constituent. The heat evolved is a latent heat of solidification. It indicates a change of internal energy *accompanied by a change of state.*

In the case of steel, on the contrary, the whole metallic mass is already in the solid state when segregation of the constituents takes place. The heat evolved here indicates a change of internal energy which is *not accompanied by a change of state.* A change of this kind is of course very suggestive, if not conclusive, of an allotropic transformation, and in it the believers in the allotropy of iron find their strongest argument.

Such considerations lead us to the notion of solid solutions. The existence of solid solutions can no longer be reasonably contested. We all know with what readiness carbon diffuses through solid steel. The phenomenon is in every way similar to the diffusion of salt in water. Many instances of solid solutions — diffusions of one metal in another, etc. — have been described recently by Professor Roberts-Austen and others.

The constitution of steel before the segregation of one of the components has begun, *i. e.*, above the curve *M E N* (Figure 3), remains to be ascertained. This region evidently corresponds to the

liquid state in metallic alloys and in saline solutions, from which it might naturally be inferred that the carbide Fe_3C is here uniformly diffused or dissolved through the iron.

It is hardly possible to examine the structure of the metal at a red heat, but by cooling the steel from one of these high temperatures very rapidly — by immersing it in cold water or in some other cooling mixture — the changes, structural and others, which take place during the retardations, do not occur, at least not in their entirety (being denied the necessary time), and we retain in the cold metal the conditions which existed at a high temperature. Such treatment constitutes the process of *hardening*, and we must ascertain the character of the constitution of *hardened* steel.

Calling the microscope to our assistance, we find that if the metal be quenched before the first retardation, unless it be very slightly or very highly carbonized, it is made up of a single constituent represented by dotted areas in the figures of Plate IV, and which has been called *martensite.* Figures 5, 8, and 11 illustrate the structure of steels containing respectively 0.21, 0.35, and 0.80 per cent. of carbon, and quenched above the curve *M E N* (Figure 3) Figure 5, Plate I, shows the structure of martensite under a magnification of 1,000 diameters. It is the reproduction of a photo-micrograph by Mr. Osmond.[1] If the metal contains very little carbon, a small amount of iron (ferrite) is found together with the martensite, even after quenching from a very high temperature. (See Figure 1, Plate IV, and Figure 6, Plate I.) In highly carbonized steel Mr. Osmond finds, upon sudden cooling from a high temperature, a new constituent which he has named *austenite.*[2] Figure 2, Plate III, shows the structure of a steel containing 1.50 per cent. carbon and quenched in ice water from a very high temperature (1,050° C.). The light background represents the austenite; the dark needles are made up of martensite.

If the metal be quenched between the first and the second evolutions of heat, it is found to be made up of a mixture of martensite and ferrite, or of martensite and cementite; the former when the metal contains less than 0.8 per cent. carbon, the latter when more highly carbonized. This is well illustrated by Figures 3, 6, 9, 13, and 15, of Plate IV. In steels quenched below the recalescence temperature no

[1] The Metallographist, Vol. I, No. 1, January, 1898.

[2] Idem.

martensite is to be found. Their microstructural compositions do not differ from those of the slowly cooled metals (Plate IV, lowest row), and we know that steel suddenly cooled from a temperature below that of recalescence is not materially hardened, if at all.

We all know that within certain carbon limits the most striking difference between the properties of steel suddenly cooled from a high temperature, and those of the same metal slowly cooled, is to be found in the enormously greater mineralogical hardness of the former. This increase of hardness it evidently owes to the presence of martensite. The statement, however, does not in any way help us to solve the problem of hardening, which has been the subject of so much investigation and so much controversy, for the cause of the hardness of martensite remains to be determined.

Martensite may be compared to the liquid portion of saline solutions and of metallic alloys. Above the curve *M E N* (Figures 1 and 2) the former are entirely liquid, while steel is made up entirely of martensite (with the exceptions noted above). Between the first and the second evolutions of heat we have in the one case crystals of one of the constituents suspended in the portion remaining liquid; in the other, crystalline particles of ferrite or of cementite imbedded in a matrix of martensite; while below the second retardation no portion of the saline solution or of the alloy remains liquid, and no martensite remains in the steel.

It is certainly reasonable to suppose that martensite is an homogeneous solid solution of carbon or of the carbide Fe_3C in iron. It can hardly be anything else. The contention that it is a definite compound of iron and carbon (to which Professor Arnold would give the formula $Fe_{24}C$) must be abandoned, for it is evident that its composition, like that of the portion remaining liquid during the cooling of metallic alloys, varies both with the composition of the steel and with the temperature.

The fact, however, even if it were conclusively established, that martensite is a solution of iron and carbon or of iron and Fe_3C, could hardly account for its extreme hardness, although certain metallurgists, the "carbonists" as they have been called, see in it a satisfactory explanation of the hardening of steel. The theory of the "allotropists," who consider martensite as a solution of carbon or of Fe_3C in an allotropic condition of the iron, itself very hard, is more plausible; it is supported by much more cogent evidences, and is steadily gaining ground.

While unhardened steel is generally made up of two of the three constituents, ferrite, cementite, and pearlyte, it may be readily conceived, however, that even if no other impurities were present, the physical properties of the steel, which give to this metal such an unique place in the arts, do not depend exclusively upon the relative proportions of these constituents — in other words, upon the carbon content; but that they depend also upon the distribution, mode of occurrence, size, and shape of the individual grains or crystalline particles, and these features are regulated by the treatment, thermal and physical, to which the metal is subjected.

The structure of steel is extremely sensitive to slight changes of treatment, and an alteration of the structure, however slight, always implies a corresponding alteration of physical properties.

The microscope gives us a means of studying those structural changes which are so closely related to the properties of the metal, and thus opens up possibilities in the art as well as in the science of metallurgy, whose value could hardly be overestimated.

THE RELIABILITY OF THE DISSOCIATION-VALUES DETERMINED BY ELECTRICAL CONDUCTIVITY MEASUREMENTS.

By ARTHUR A. NOYES.

1. *Van Laar's Correction of the Heat of Solution Formula.*

There has recently appeared[1] an article by van Laar in which he claims with the greatest positiveness that the dissociation-values calculated from the electrical conductivity are incorrect. In order to sustain this view, he brings forward certain "proofs" and offers an hypothesis concerning the cause of the supposed unreliability of the conductivity method. The matter is of so great importance and the view of van Laar is, in my opinion, so completely unjustifiable, that I feel compelled to reply to his arguments, and to present the existing proofs of the contrary idea.

As an evidence of his view, van Laar attempted to show that the heats of solution calculated thermodynamically from the changes in solubility caused by variations of temperature agreed much better with the experimental values when the theoretical (Ostwald) dilution-law was used in the calculation, than when the empirical (Rudolphi-van't Hoff) law derived from conductivity values was employed. Unfortunately, however, van Laar has not, it seems to me, derived correctly the relation between the change in solubility and heat of solution in the case of dissociated substances. It is apparent that his equation in the derivation of which the empirical dilution-law was assumed is incorrect, since this furnishes an evidently false result in the limiting case of complete dissociation. The equation to which I refer is as follows:

$$\frac{L}{RT^2} = \frac{3}{3-a}\,\frac{d\log s}{dT} \qquad (1),$$

in which L expresses the heat of solution; R, the gas constant; T,

[1] Ztschr. phys. Chem., 21, 79.

the absolute temperature, a the degree of dissociation, and s the solubility. When $a = 1$, this equation becomes:

$$\frac{L}{RT^2} = \frac{3}{2}\frac{d\log s}{dT} \qquad (2).$$

For complete dissociation, however, this equation must evidently be quite independent of any dilution-law whatever; for no change in the degree of dissociation takes place in this case. Also, since in the case of a wholly dissociated di-ionic salt the equilibrium constant K, which occurs in the general van't Hoff equation:

$$\frac{d\log K}{dT} = \frac{Q}{RT^2},$$

is equal to s^2, the product of the concentrations of the ions, it follows that:

$$\frac{L}{RT^2} = \frac{2\,d\log s}{dT}, \qquad (3),$$

an equation which has already[1] been employed and confirmed. Even the equation derived by van Laar under the assumption of the theoretical dilution-law,

$$\frac{L}{RT^2} = \frac{2}{2-a}\frac{d\log s}{dT} \qquad (4),$$

becomes simplified to equation (3), when $a = 1$. His two equations (2) and (4) therefore lead to different results in the case where the influence of the dilution-law must disappear. Moreover, even the last equation of van Laar cannot be correct in general, although it fulfils the conditions of the two limiting cases; for it contains no term which represents the change of the dissociation with the temperature. This is, however, obviously necessary; for the heat of solution of a partially dissociated substance may be regarded as the sum of two quantities, one of which depends on the heat of solution of the undissociated substance, and the other on its heat of dissociation. This latter amount of heat is, however, determined thermodynamically by the temperature-change of the dissociation-constant, while the former is independent of it. Accordingly the sum, the actual heat of solution, must be a function of the temperature-change of the dissociation.

[1] Nernst, Theoretische Chemie, 516.

The original equation of van't Hoff[1]

$$\frac{L}{RT^2} = \frac{i\,d\log i\,s}{d\,T} = (1+a)\,\frac{d\log s}{d\,T} + \frac{d\,a}{dT} \qquad (5)$$

satisfies this theoretical requirement. That of van Laar is an attempted improvement on this. According to him the assumption of van't Hoff[2] and Rudolphi[3] that: $L = W + a\,Q$, where L is the actual (total) heat of solution; W, the heat of solution of the undissociated substance, and Q, its heat of dissociation, is not correct; but since in the solution of the quantity ds there takes place, besides its own change in dissociation, a change in the degree of dissociation of the total quantity s of the substance present, by an amount $\frac{da}{ds}\,ds$, it follows that $L\,ds = W\,ds + (a + s\,\frac{da}{ds})\,Q\,ds$, in which the quantity $\frac{da}{ds}$ is to be obtained from the dilution-law. For the heat of solution, L, of a gram molecule, it follows, therefore, according to van Laar, that: $L = W + (a + s\,\frac{da}{ds})\,Q$.

This "correction" seems to me, however, to be wholly erroneous, and to arise from a misunderstanding of the significance of the heat of solution. The molecular heat of solution is, in a thermodynamical sense, the heat which is absorbed by the dissolving of one molecule of the substance in a solution of *unchangeable* concentration; namely, that corresponding to the equilibrium. Even differential changes of concentration must not occur if the thermodynamic relations are to hold strictly; and if they actually occur, as van Laar assumes, the heat of solution then obtained will differ from the thermodynamical heat by an amount corresponding to the influence of those changes in concentration. That is to say, the dissolving must take place with a simultaneous increase in the volume of the solution by the addition of the solvent, in such a way that the concentration remains constant, just as in the reversible evaporation of a liquid the volume of the vapor must increase continuously.

By these considerations it seems to me that the falsity of van Laar's attempted correction of van't Hoff's equation is made evident. The matter is, however, so important, as well from a general point of

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[1] Ztschr. phys. Chem., 17, 147; $i = (1 + a)$ for a di-ionic electrolyte.
[2] Ztschr. phys. Chem., 17, 547. [3] Ztschr. phys. Chem., 17, 299.

view as from the standpoint of this discussion, that it seems proper to present a direct derivation of the van't Hoff equation by means of a cyclical process, and especially so, since van't Hoff himself, according to the assertion of van Laar,[1] has acknowledged the validity of the latter's proposed correction.

2. *Derivation of the Relation Between the Heat of Solution of Dissociated Substances and the Change in their Solubility with the Temperature.*

In order to derive this relation we will consider a cyclical process to be carried out by means of an osmotic machine. The machine consists, in its original condition, of a cylinder provided with a semi-permeable piston, in the bottom of which, below the piston, is one molecule of the solid substance, while above is that amount of the pure solvent in which the solid substance is soluble. The solid substance is moistened with an infinitely small amount of the saturated solution, and the osmotic pressure on the piston is just balanced by a corresponding weight. The machine is placed in a very large heat reservoir at $T°$, and the following cyclical process consisting of five parts is carried out:

Part I. By an indefinitely small decrease of the weight on the piston the latter is allowed to rise until the solid substance is dissolved. Let the concentration of the resulting saturated solution be expressed by s.

Part II. The piston is fastened and the machine placed in a very large heat reservoir at $(T + dT)°$.

Part III. The piston is set free after loading it with a weight equal to the osmotic pressure; the weight is then increased by an indefinitely small amount, and the piston allowed to sink until the concentration of the solution has risen from s to that of the solution saturated at $T + dT$, that is, $s + ds$.

Part IV. The piston is now allowed to sink still further, until the molecule of the substance has separated out of the solution.

Part V. Finally the machine is placed in the heat reservoir at $T°$.

The cyclical process is now completed and the original condition restored. The Second Law of Energetics gives now the relation which must exist between the work dA performed on the system and

[1] Ztschr. phys. Chem., 17, 547.

the amount of heat Q which is transferred from one temperature to the other. This relation is: $dA = Q\frac{dT}{T}$. (6).

We will next determine the amount of work performed in the above-described process. The work done in each part consists in a change of volume taking place at a constant pressure, and is therefore equal to the product of these two quantities. According to the *Avogadro-van't Hoff* principle, the osmotic pressure is equal to nRT, where n denotes the number of molecules present. As above, the concentration of the solution saturated at $T°$ is s, and at $T + dT°$ is $s + ds$. Further, let the number of molecules which is present in the solution of one molecule of the solid substance at $T°$ be i, and at $T + dT°$ be $i + di$. Then the following values of the change in volume ($\triangle v$), of the pressure (P), and of the work performed (A), in the separate parts of the process, are:

Part I. $(\triangle v)_{\text{I}} = \frac{1}{s}$; $P_{\text{I}} = isRT$; $A_{\text{I}} = -iRT$.

Part II. $(\triangle v)_{\text{II}} = 0$; $A_{\text{II}} = 0$.

Part III. $(\triangle v)_{\text{III}} = -\left(\frac{1}{s} - \frac{1}{s + ds}\right)$; $P_{\text{III}} = is\,R\,(T + dT)$;
$A_{\text{III}} = iRT\,d\,log\,s$.

Part IV. $(\triangle v)_{\text{IV}} = -\frac{1}{s + ds}$; $P_{\text{IV}} = (i + di)(s + ds)\,R\,(T + dT)$;
$A_{\text{IV}} = iRT + iRdT + RT\,di$.

Part V. $(\triangle v)_{\text{V}} = 0$; $A_{\text{V}} = 0$.

The total work done in the process is therefore:

$$dA = iR\,(T\,d\,log\,is + dT).$$

On the other hand the amount of heat, Q, absorbed at the temperature T is evidently the sum of the heat of solution L in the ordinary sense (without work being done) and the external work; that is to say, $Q = L + iRT$. If these values of dA and Q are substituted in equation (6), the expression of the Second Law, we obtain $\frac{L}{RT^2} = \frac{i\,d\,log\,is}{dT}$, which is the original van't Hoff equation. Attention may be especially called to the fact that in this cyclical process no opportunity is offered for the introduction of van Laar's correction. These equations are evidently independent of any dilution-law whatever, and of the

number of ions into which the electrolyte is dissociated. If the electrolyte breaks up to an extent a into n ions, $i = 1 + (n - 1)\,a$, whence follows:

$$\frac{L}{RT^2} = [1 + (n - 1)\,a]\,\frac{d\,log\,s}{dT} + (n - 1)\,\frac{da}{dT}.$$

Now if the electrolyte follows the dilution-law: $K = \frac{(a\,s)^{\nu}}{(1 - a)s}$

where ν may have any value, then we obtain by differentiation:

$$\frac{da}{dT} = \frac{a\,(1 - a)}{\nu - (\nu - 1)a}\,\frac{d\,log\,K}{dT} - \frac{(\nu - 1)\,a\,(1 - a)}{\nu - (\nu - 1)a}\,\frac{d\,log\,s}{dT}.$$

By substitution of this value in equation (6) we obtain:

$$\frac{L}{RT^2} = \frac{\nu + (n - \nu)a}{\nu - (\nu - 1)a}\,\frac{d\,log\,s}{dT} + \frac{(n - 1)\,a\,(1 - a)}{\nu - (\nu - 1)a}\,\frac{d\,log\,K}{dT} \quad (7).$$

This equation is rigidly exact and general; in it we presuppose only that the electrolyte follows some exponential dilution-law of the assumed form.

In the two limiting cases where $a = 1$, and $a = 0$, the equation becomes simplified to:

$$\frac{L}{RT^2} = \frac{n\,d\,log\,s}{dT}, \text{ and } \frac{L}{RT^2} = \frac{d\,log\,s}{dT},$$

as the theory requires. In general, however, in the calculation of the heat of solution, a knowledge not only of the temperature-change of the solubility, but also that of the dissociation-constant, is necessary. The latter change has in the case of most electrolytes been shown to be so small that for practical purposes the last member may ordinarily be neglected without a large error, a simplification which is permissible especially in the case of very weakly and very strongly dissociated electrolytes, for the coefficient of $d\,log\,K : dT$ disappears when a approaches zero or unity.

We will now consider two special cases: first, where the electrolyte is di-ionic and follows the theoretical (Ostwald) dilution-law, where it is, for example, a weak acid or base; and second, where the electrolyte is di-ionic and follows the empirical (van't Hoff) dilution-law, where it is, for example, a salt. In both cases $n = 2$; in the first

case $\nu = 2$, and in the second $\nu = \frac{3}{2}$. By substituting these values in equation (7) and omitting the last member we obtain:

$$\frac{L}{RT^2} = \frac{2}{2 - a} \frac{d \log s}{dT} \quad \text{when } \nu = 2 \qquad (8).$$

and $$\frac{L}{RT^2} = \frac{3 + a}{3 - a} \frac{d \log s}{dT} \quad \text{when } \nu = \frac{3}{2} \qquad (9).$$

The first formula is identical with that obtained by van Laar; the second is, however, essentially different from his, which reads:

$$\frac{L}{RT^2} = \frac{3}{3 - a} \frac{d \log s}{dT} \qquad (10).$$

3. *Comparison of the Calculated and the Observed Heats of Solution.*

In the following tables the results of the calculation of the heats of solution according to the three formulæ (8), (9), and (10), given above, are placed together beside the experimentally found values for the four substances used by van Laar. Only those values in the next to the last column are calculated by me;[1] the rest are those of van Laar.

HEATS OF SOLUTION.

	Ostwald's dilution-law assumed. Calculated by (8).	Van't Hoff's dilution-law assumed.		Experimentally found.
		Calculated by (10).	Calculated by (9).	
Silver acetate	4369	3688	4562	4613
Silver propionate . . .	3789	3148	3928	3980
Silver isobutyrate . . .	2715	2289	2836	2860
o-Nitrobenzoic acid . .	7167	6766	7449	7083

From the fact that the values in the first column of numbers, which were obtained with the help of the Ostwald law, agree much more closely with the experimental values than do those of the second

[1] These values were obtained from those of van Laar in the preceding column by multiplication by $\frac{3 + a}{3}$. The values of a used are those derived by van Laar from conductivity measurements, namely: for silver acetate, 0.713; for silver propionate, 0.744; for silver isobutyrate, 0.718; and for *o*-nitrobenzoic acid, 0.303.

column, which were calculated by means of van't Hoff's dilution-law and the equation of van't Hoff as corrected by van Laar, van Laar concluded that salts in reality follow Ostwald's dilution-law, and not van't Hoff's, as is to be inferred from the conductivity; in other words, the conductivity gives, according to him, incorrect values of the dissociation. Further support of this latter assumption he finds in the fact that in the case of the three salts, even the values calculated with the help of Ostwald's law differ from the experimental ones by several per cent. But I have proved above, as I believe, that the equation of van Laar, in the deduction of which van't Hoff's dilution-law was presupposed, is incorrect, and that the true expression is equation (9). If one is to decide between the two dilution-laws, the values of the first and *third* columns of numbers must, therefore, be compared with those of the fourth. This comparison shows now just the opposite result: in the case of the three salts, the values deduced from van't Hoff's law agree almost completely (within 0.8 to 1.3 per cent.) with the actual ones, while those from Ostwald's law deviate by about 5 per cent. Moreover, it is especially worthy of note that the nitrobenzoic acid, which like all weak acids follows Ostwald's law, possesses a heat of solution which is in accord with the assumption of the validity of this law, but which is not consistent with van't Hoff's law. The results are therefore in perfect agreement with the usual assumptions based on conductivity in regard to the dissociation of the substances in question, and not only is the argument of van Laar refuted, but at the same time a new proof is furnished of the validity of van't Hoff's dilution-law in the case of salts, and of the reliability of the dissociation-values determined from conductivity measurements.

4. *Electrical Conductivity and Inversion Velocity in Mixtures of Water and Alcohol.*

Van Laar finds a further proof of his view in the fact that the rate of the inversion of sugar by hydrochloric acid, in mixtures of alcohol and water, is essentially different from that in pure water, although according to Cohen[1] the degree of dissociation of the acid, as determined by its conductivity in the two solvents, is the same. Cohen[2] also considers this fact as leading to the conclusion that "in solutions in mixtures of water and alcohol the electrical conductivity is not an entirely correct measure of the degree of dissociation."

[1] Ztschr. phys. Chem., **25**, 41. [2] Ibid, p. 44.

It is remarkable that this conclusion has been drawn by two separate investigators; for it appears to me obviously unjustified. Even if the concentrations of the hydrogen ions are the same, it is by no means to be expected that the rates of inversion in the different solvents would be equal. For, aside from the fact that the catalytic activity of the hydrogen ions is not necessarily constant, it is clear that the concentration of one of the reacting substances, the water, undergoes a change; and it would be indeed remarkable if this change had no influence on the rate of inversion. It is not improbable that the ions of the water play an important part in the hydrolysis of the sugar, and it has been shown by Löwenherz[1] that the addition of alcohol greatly reduces the dissociation of water. It is therefore entirely inadmissible to ascribe to the inversion results such a significance as van Laar and Cohen do.

5. *Van Laar's "Explanation of the Deviations from Ostwald's Law."*

It seems superfluous to discuss the hypothesis of van Laar on the cause of the incorrectness of the dissociation-values derived from the conductivity, since, from what has been said above, no reason exists to doubt their correctness. A remark in regard to it may be, however, not without interest. If I correctly understand his hypothesis, its essential feature is that the Joule heat-effect, which is continuously produced by the current during the measurement of the conductivity, causes a localized increase of temperature around the ions, as a result of which the dissociation is temporarily changed. Against this hypothesis, however, there exists the following fatal objection: if the dissociation and conductivity are affected by the heat produced by the current, then the observed values of these would depend on the strength of current employed, which is known not to be the case.

6. *Existing Determinations of the Dissociation by Independent Methods.*

In his article, van Laar pays no attention to the previously published experiments which bear upon the reliability of the conductivity method of determining dissociation; yet certain investigations have been carried out, the purpose of which was to answer this very question. In the first place may be considered the recent investigations of

[1] Ztschr. phys. Chem., **20**, 294.

Jones,[1] Loomis,[2] Abegg,[3] and Raoult,[4] on the lowering of the freezing-point of water by certain salts. Of these the two salts, potassium chloride and sodium chloride, have been most carefully studied; for the lowerings of freezing-point caused by them have been determined by all four of the mentioned investigators.

In order to show now the extent of the agreement of the values with one another and with the results of the conductivity method, I have brought together in the following table the calculated dissociation-values for the concentrations 0.01 to 0.1 normal. In the calculations from the freezing-point-lowerings 1.85° was assumed as the molecular lowering of water.[5] The conductivity determinations of Kohlrausch were made use of in calculating the dissociation-values by this method.

DISSOCIATION-VALUES.

Normal concentrations.	Potassium Chloride.						Sodium Chloride.					
	Jones.	Loomis.	Abegg.	Raoult.	Mean.	Kohlrausch.	Jones.	Loomis.	Abegg.	Raoult.	Mean.	Kohlrausch.
0.01	95	95	96	..	95.3	94.4	95	99	105	..	99.7	93.7
0.03	92	90	90	91	90.8	91.1	92	93	92	97	93.5	89.6
0.05	90	89	88	88	88.8	89.1	90	91	92	93	91.5	87.3
0.10	87	86	..	85	86.0	86.2	88	88	88	89	88.2	84.2

It is seen that, in the case of potassium chloride, the four separate values by the freezing-point method agree well with one another; and the averages of them are almost identical with the dissociation-values calculated from Kohlrausch's conductivity measurements. In the case of sodium chloride, however, the agreement between the freezing-point results of the separate observers is not so complete, and their averages are about 4 per cent. higher than the values to which

[1] Ztschr. phys. Chem., **11**, 110, 529; **12**, 623.
[2] Wied. Ann., **51**, 500; **57**, 495.
[3] Ztschr. phys. Chem., **20**, 207.
[4] Comptes rendus, **124**, 885; 125, 751.
[5] Compare Abegg., Wied. Ann., **64**, 499.

the conductivity leads. Whether this latter result arises from a constant error in the freezing-point determinations or from a theoretical inaccuracy in one of the two methods can not, of course, be determined at present. In view of this fact it must be admitted, to be sure, that these freezing-point measurements do not contribute much towards answering the question regarding the reliability of the conductivity method. Nevertheless a certain significance is to be attributed to the close agreement in the case of the potassium chloride, the best investigated salt.

In another way, however, more decisive evidence of the reliability of that method has been furnished. From the phenomenon of solubility effect it is possible to determine dissociation-values, and experiments of Noyes and Abbot[1] have shown that the values so determined in the case of certain thallium salts are in accordance with those derived from the conductivity. For details reference is made to the original article; but the final results may be presented here. The first two columns of figures in the following table show the dissociation-values which were calculated from independent solubility experiments with two pairs of salts. The last column contains the corresponding dissociation-values, which were derived from the conductivity.

Salt.	From solubility experiments. I.	From solubility experiments. II.	From the conductivity.
Tl Cl	86.5	86.5	86.6
Tl SCN	86.7	86.6	85.6
Tl Br O_3	89.9	91.1	89.0

These entirely distinct methods, freezing-point-lowering and solubility-effect, lead therefore to nearly the same dissociation-values. That the electrical conductivity furnishes essentially correct dissociation-values in the case of di-ionic salts in moderately dilute solution is therefore probable. At any rate, more weighty reasons than those brought forward by van Laar must be discovered, before this method should be discredited.

[1] Ztschr. phys. Chem., **16**, 136.

EXPERIMENTAL STUDY OF TRANSFORMER DIAGRAMS.

By HARRY E. CLIFFORD, NATHAN HAYWARD, and ROBERT ANDERSON.

The method of graphically representing the various currents and electromotive forces concerned in two mutually related circuits has been most beautifully and extensively developed by Bedell.[1] For two such circuits, in one of which, the primary, a constant periodic current is caused to flow, the loci of primary impressed voltage and secondary current and electromotive force, when the secondary resistance is varied, are shown in Figure 1. To pass to the case in which the electromotive force impressed on the primary circuit is constant, requires a mere alteration in length of every line in the diagram, in a ratio which is readily determined for a given primary E. M. F. The character of the necessary changes in the original diagram will be at once appreciated from a consideration of Figure 2. The effect of magnetic leakage or external inductance in the secondary circuit is to cause a displacement of

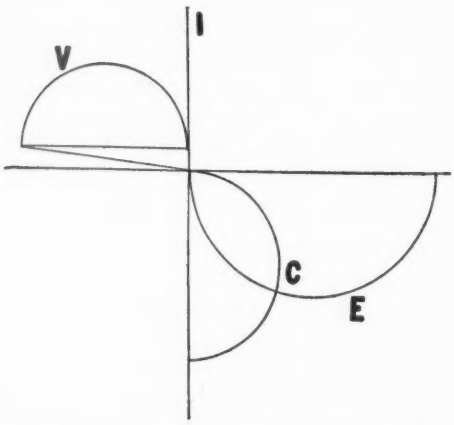

Fig. 1.—Transformer Diagram with Constant Current in the Primary.

V = Locus of vectors representing primary impressed E.M.F. at different loads.
E = Locus of vectors representing voltage across the secondary at different loads.
C = Locus of vectors representing secondary current at different loads.
I = Vector representing primary current.

All phases are measured from I, the clock-wise direction being taken as positive for lag. All vectors are in the extreme left-hand position at no load; moving in the clock-wise direction as the load comes on.

[1] Bedell. Principles of the Transformer.

the locus of the primary E. M. F. from the locus of the primary current. This effect is well illustrated in Figure 3.

It seems somewhat strange that the relations indicated by these various transformer diagrams should have received no especial attention from the standpoint of experimental verification — the only tests, so far as we are aware, being those carried on by Bedell,[1] in which there is, as it seems to us, one serious error. Throughout his work it is assumed, without measurement, that the secondary E. M. F. is 90° behind the primary current — an assumption which is hardly justifiable in the light of our results.

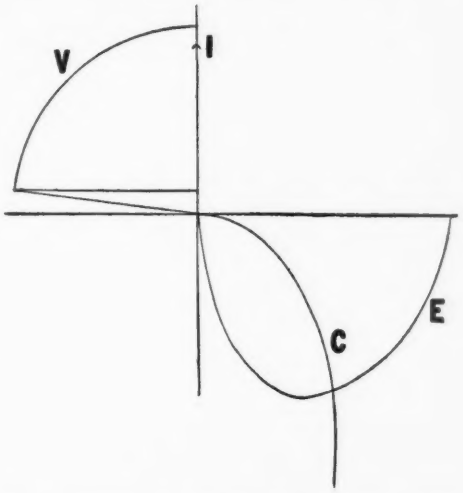

FIG. 2. — TRANSFORMER DIAGRAM, WITH CONSTANT E.M.F. IMPRESSED ON PRIMARY.

V = Locus of vectors representing primary E.M.F. at different loads.
E = Locus of vectors representing voltage across secondary at different loads.
C = Locus of vectors representing current in secondary at different loads.
I = Direction of vector representing primary current; the length of vector being a variable.

As our work demanded a transformer in which the magnetic reluctance and magnetic leakage could be changed through wide limits, we chose a modified Ferranti type, in which the coils could be placed in any relative position, the core removed or used with either open or closed magnetic circuit. To accomplish this the primary was wound on a bobbin, into which the core would just fit: the secondary slipped over the primary. The core was built up of seventy-three mild steel stampings 20″ x 2.5″ of the kind used by the General Electric Company in the modern "H" transformer, and when placed in position might be left either unbent, as in a hedgehog transformer, or bent into a more or less compact magnetic circuit. We were thus able to vary

[1] Proceedings of International Electrical Congress held at Chicago, 1893, p. 234.

the magnetic reluctance from that of an air transformer to that of a commercial Ferranti transformer, and at each step vary the leakage by changing the relative position of the coils. We stepped up by a ratio of 4 to 1, using a bank of lamps as our load, which we assumed to be non-inductive.

The primary current was measured by the ordinary type of Siemen's dynamometer of a range from 0.5 to 20 amperes. The dynamometer was calibrated by means of Weston ammeters. The voltages, both primary and secondary, were determined with an electrostatic voltmeter having a range from 30 to 150 volts. The range of the voltmeter necessitated the use of a non-inductive drop in the secondary circuit, but the use of this enabled the instrument to be read in the most precise portion of the scale. Calibration of these instruments was made with a Weston voltmeter. The phase angles were determined by the ordinary contact method,[1] measuring the angles between the zero points. When the wave was distorted by hysteresis, the lag angle was obtained from the power factor. The frequency was determined by comparison with a König standard fork, the dynamo being found to vary comparatively little throughout the entire time of the experiments, and to give very closely a sine wave of electromotive force.

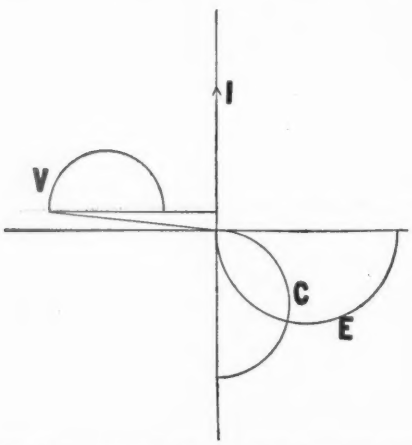

FIG. 3.—TRANSFORMER DIAGRAM, WITH CONSTANT CURRENT IN PRIMARY, AND EITHER EXTERNAL SELF-INDUCTANCE OR MAGNETIC LEAKAGE IN SECONDARY.

V = Locus of vectors representing primary E.M.F.
(The semi-circle has been moved away from vector I.)
E = Locus of vectors representing secondary E.M.F.
C = Locus of vectors representing secondary current.
I = Vector representing primary current.

CONSTANT CURRENT AIR TRANSFORMER.

The first series of tests was carried on without the use of the iron core, the secondary coil being placed directly over the primary. The

[1] Electrical World, Vol. xviii, p. 141, August 29, 1891.

inductances of the coils were determined by the Wheatstone bridge method of comparison with a known variable inductance.

Owing to the fact that in this run the values were not within the ranges of our instruments, the primary current and the primary and secondary electromotive forces were determined from the plot taken by the contact method, the ordinates being measured at twelve points, and the square root of the mean square found. A summary of the results of this test is given in the following table:

TABLE I.

	Effective Values.				Phase with Respect to P. C. of	
Loads.	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	9.17	32.4	14.2	....	−77.4°	+96.0°
1st . .	9.11	31.4	14.2	.342	−71.1°	+107.4°
2d . .	8.32	22.9	14.2	.832	−68.4°	+132.6°
3d . .	6.90	8.38	14.2	1.20	−67.8°	+161.4°
4th . .	6.52	3.29	14.2	1.22	−67.2°	+170.4°
5th . .	6.44	1.17	14.2	1.22	−70.5°	+174.9°

It is to be observed that the current is kept constant throughout the test. A no-load run could not be made, as the contact method required us to use a drop across our secondary. This, however, was allowed for in diagram. A correction was also made for the primary drop.

The effect of magnetic leakage is clearly shown in the following diagram, Figure 4, in which the plotted points represent the experimental results, the continuous lines indicating the theoretical polar diagram. Considering the fact that a precision closer than 2 per cent. could hardly be hoped for in the measurements themselves, it seems reasonable to conclude that the air transformer follows the theoretical constant current diagram with great exactness.

Constant Electromotive Force in Primary.

A series of tests was next conducted with the coils arranged as at first, but with the iron core introduced in the hedgehog form, and the

primary E. M. F. kept sensibly constant at 49 volts. A summary follows in Table II:

TABLE II.

	Effective Values.				Phase with Respect to P. C. of	
Loads.	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	48.9	179.	8.17	....	−85.5°	+ 96°.
1st . .	48.9	174.	9.50	1.02	−66.6°	+123°.
2d . .	49.0	169.	11.42	1.76	−52.5°	+137°.
3d . .	49.5	166.	13.37	2.34	−48.3°	+147°.
4th . .	49.0	158.	15.68	3.00	−45.0°	+153°.
5th . .	49.0	152.	17.75	3.57	−43.6°	+157°.

The graphical representation of this series is shown in Figure 5. Although no comparison can be made with the theoretical diagram, the form of the curves is at once seen to be similar to that which would be expected from the theory itself, and which is illustrated in general by the diagram, Figure 2. A second series was next taken with the core precisely the same as in the preceding tests, but the coils slipped apart instead of being one directly outside the other.

TABLE III.

	Effective Values.				Phase between P. C. and	
Loads.	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	45.1	147.	7.77	....	−83.5°	97°.
1st . .	45.1	140.	8.73	.79	−68.9°	122°.
2d . .	45.3	132.	10.18	1.35	−62.2°	139°.
3d . .	45.0	126.	11.45	1.72	−60.5°	146°.
4th . .	44.9	100.	14.47	2.58	−61.2°	159°.

The graphical representation of this series, Figure 6, is of course similar to that shown in Figure 5, and is of interest as evidencing very strongly the effect of increased magnetic leakage. With this type of

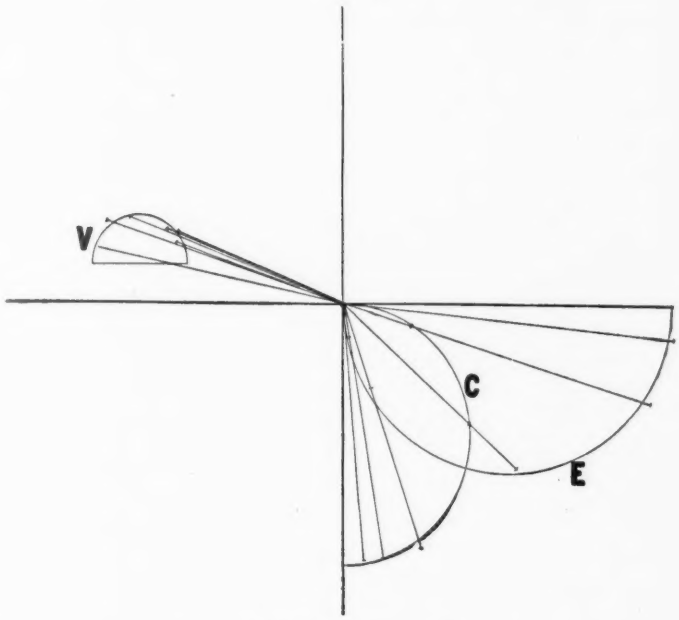

FIG. 4. — AIR TRANSFORMER.
V = Locus of primary E.M.F. E = Locus of secondary E.M.F. C = Locus of secondary current.

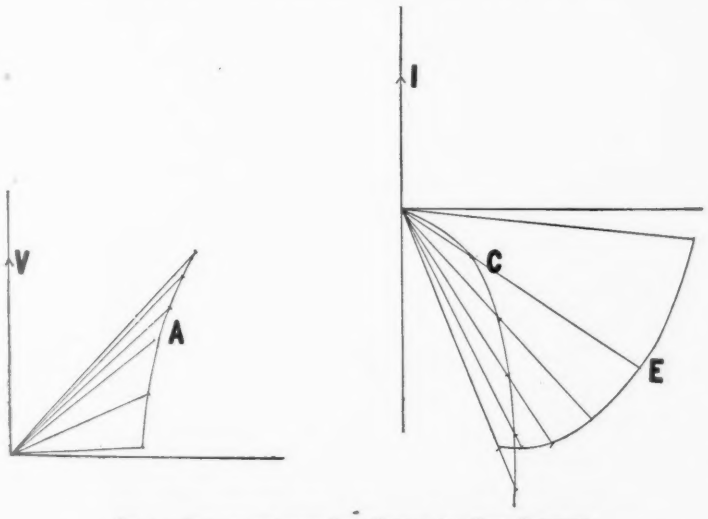

FIG. 5. — TRANSFORMER WITH CORE UNBENT AND COILS TOGETHER.
C = Locus of the current in secondary; the phase measured from primary current "I."
E = Locus of the E.M.F. in secondary; the phase measured from primary current "I."
A = Locus of the current in primary, the phase measured from primary E.M.F. "V."
(These are direct plots of the observed values, the clock-wise direction being taken as the direction of lag.)

transformer the current wave was not sensibly distorted from its sine form. From this fact we should expect no distortion of the polar diagram. In order to see if this is the case, we have reduced by direct ratio Figures 5 and 6 to constant current diagrams, and superimposed one on the other in Figure 6 (a). These two diagrams, like that in Figure 4, seem to show most conclusively that the theory sensibly holds for a transformer of this type. The effect of magnetic leakage is here shown most satisfactorily. The larger semicircles represent the values with the coils together, the smaller those with coils apart.

Closed Magnetic Circuit.

The core was next bent to form a closed magnetic circuit, giving a loop of such size that the coils might be arranged to show the effect of leakage to a greater or less extent. In this series of tests hysteresis comes into play to a marked degree, causing a distortion of the primary current wave, and producing a change in the phase relations of primary and secondary electromotive force. The lag angle in the

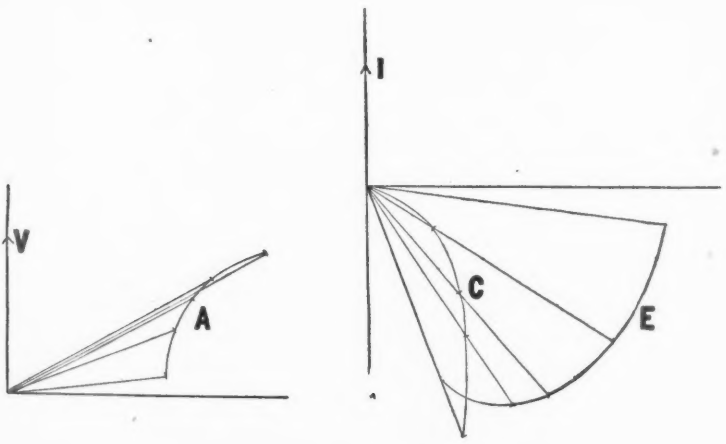

Fig. 6.—Transformer with Core Unbent and Coils Apart.

C = Locus of the current in secondary; the phase measured from primary current "I."
E = Locus of the E.M.F. in secondary; the phase measured from primary current "I."
A = Locus of the current in primary; the phase measured from the E.M.F. of primary "V."

(These are direct plots of the observed values; the clock-wise direction being taken as the direction of lag.)

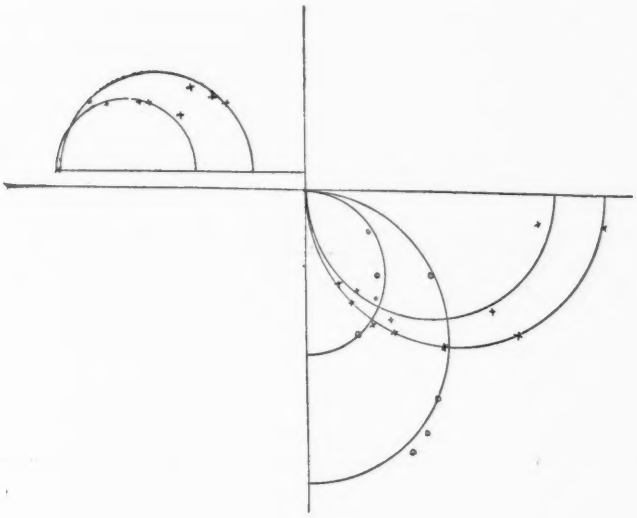

FIG. 6 (a).

(Figures 5 and 6 reduced to constant current.)

The larger circles are obtained from 5, the smaller from 6. The circles are drawn as the ones best representing the points obtained from 5 and 6.

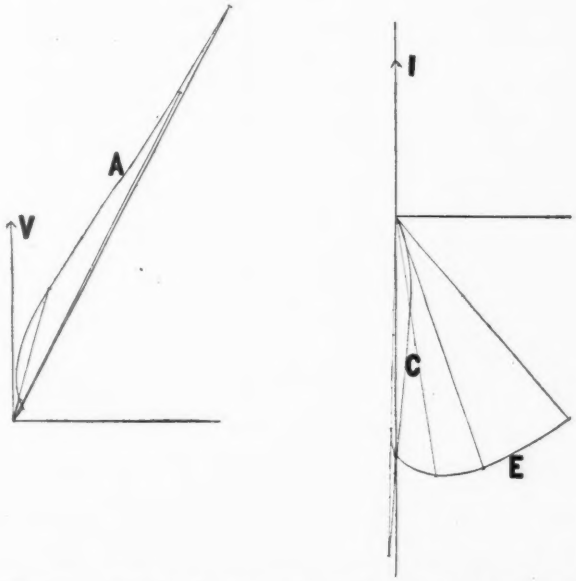

FIG. 7.—TRANSFORMER WITH CORE BENT INTO A CLOSED MAGNETIC CIRCUIT AND COILS TOGETHER.

A = Locus of the primary current; the phase measured from primary voltage "V."
C = Locus of the secondary current; the phase measured from primary current "I"
E = Locus of the secondary E.M.F.; the phase measured from primary current "I."

(These are direct plots of the observed values; the clock-wise direction being taken as the direction of lag.)

primary circuit was consequently determined from the power factor deduced from the watt curve. A summary of these results is given in Table IV, and the graphical result is shown in Figure 7.

TABLE IV.

	Effective Values.				Phase between P. C. and	
Loads.	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	46.8	192.	.41	0	−41°.	138°.
1st . .	47.2	192.	.56	.096	−21°.	159°.
2d . .	47.1	187.	4.92	1.10	−16°.	171°.
3d . .	46.8	170.	13.33	3.08	−28°.−	180°.
4th . .	46.8	152.	17.00	4.07	−28.°+	181°.

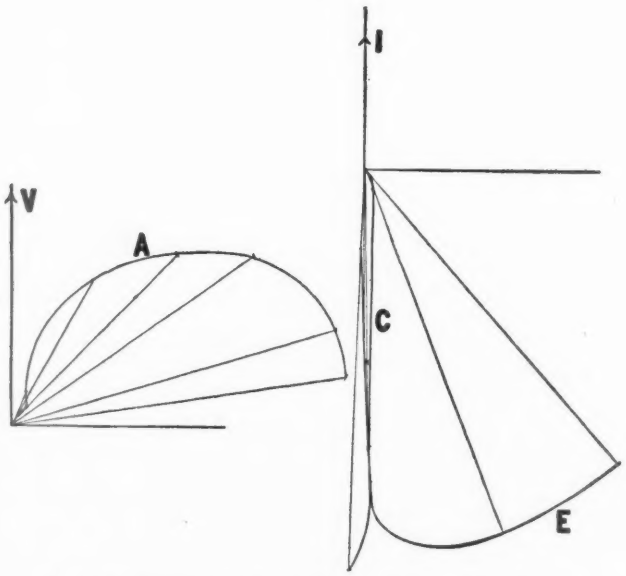

Fig. 8.—Transformer with Closed Magnetic Coils at Right Angles.

C = Locus of the secondary current; the phase measured from primary current "I."
E = Locus of the potential across secondary; the phase measured from primary current "I."
A = Locus of the primary current; the phase measured from primary voltage "V."

(These curves are direct plots of the observed values; the clock-wise direction taken as direction of lag.)

It will be observed that although the theoretical diagram is followed to a certain extent, yet the distortion is very marked. It will be noticed that the lag of secondary E. M. F. with reference to the primary current is no longer 90° on open secondary, but 138°, which effect is undoubtedly to be ascribed to hysteresis. The distortion of the current wave is also much more marked when no load is present than at full load.

Keeping the magnetic circuit constant in character, the coils were next moved so as to occupy planes at right angles to each other, thus increasing the leakage. Table V gives a summary of the results when the coils were in this position.

TABLE V.

	Effective Values.				Phase between P. C. and	
Loads.	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	46.6	192.	.407	0	—42°.	139°.
1st . .	46.6	188.	.88	.094	—25°.	158°.
2d . .	46.1	163.	4.05	.93	—29°.	179°.
3d . .	46.3	150.	5.75	1.34	—44°.	178°.
4th . .	46.7	133.	7.20	1.68	—55°.	178°.
5th . .	45.5	38.	8.25	1.93	—74°.	182°.
6th . .	45.5	....	8.25	Short circuit.	—82°.	182°.

It is very interesting to observe in the graphical representation of the results of this test, Figure 8, the peculiar form for the primary current curve, differing as it does from the form obtained in any of the previous tests, and indicating the nature of variation of the primary current in those transformers whose secondaries may be safely short-circuited.

As a final test it was decided to bring the transformer into as nearly a practical form as possible. Over four pounds (29 per cent.) of iron were removed from the core, which was then made in the closed circuit form, the coils being placed one directly over the other, the arrangement being a good Ferranti transformer. The tests were conducted exactly as in the two immediately preceding cases. Summary and graphical representations are shown in Table VI and Figure 9.

TABLE VI.

Loads.	Effective Values.				Phase between P. C. and	
	P. E.	S. E.	P. C.	S. C.	P. E.	S. E.
No. . .	46.7	....	.396	....	−55°.	+125°.
1st . .	47.0	202.	.652	.115	−19°.	+162°.
2d . .	46.8	185.	4.55	1.079	−13°.	+174°.
3d . .	46.8	174.	10.05	2.34	−22°.	+174°.
4th . .	46.8	149.	16.8	4.02	−31°.	+176.°

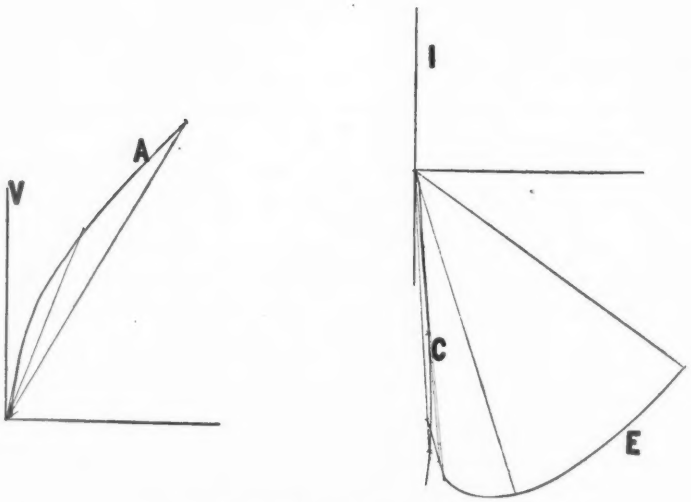

Fig. 9. — Ferranti Transformer.

C = Locus of secondary current; the phase measured from "I."
E = Locus of voltage across secondary; the phase measured from "I."
A = Locus of primary current; the phase measured from primary E.M.F. "V."

(These curves are direct plots of observed values; the clock-wise direction being taken as direction of lag.)

It is of some interest to observe the diminished distortion in this particular diagram, due, without doubt, to the lessened effect of hysteresis, owing to the removal of a portion of the iron forming the magnetic circuit. It will also be observed that the lag of secondary E. M. F. with respect to primary current has been reduced from 138° to 125°, as one would expect.

If we now compare the last three figures with Figure 2, we see how much they are distorted from the theoretical, while as we have seen in the first three cases the distortion, if any, is negligible. This distortion, therefore, appears first when hysteresis begins to have its effect in altering the sine wave of primary current, and what is more, the distortion increases as the effect of hysteresis increases. We therefore feel safe in assuming that this distortion is due to hysteresis.

If we compare Figures 7, 8, and 9 with 2, we see that the secondary diagram is not only revolved in the clockwise direction, but is shut up, *i. e.*, the no-load vector is revolved further than the full-load. This is what we should expect, as at no-load the hysteresis effect, as shown by distortion of the primary current curve, is much greater than at full-load.

ROGERS LABORATORY OF PHYSICS.
December, 1897.

ON THE BEST RESISTANCE FOR A SENSITIVE GALVANOMETER.[1]

By FRANK A. LAWS.

It is well known that in the practice of most methods of electrical testing, the precision attainable depends on the proper adjustment of the galvanometer resistance to the work in hand, and that in planning new work a solution for the best galvanometer resistance is always made. It is our purpose to derive a solution under conditions other than those usually imposed.

To render the discussion more complete, a statement of the usual solution of the problem will be given. It is as follows: If a simple circuit, consisting of a battery, a resistance and a galvanometer, be arranged, the deflection of the instrument will be a maximum when the galvanometer resistance is equal to that of the remainder of the circuit. In obtaining this solution two assumptions are made:

First. That the coils have fixed dimensions.

Second. That the ratio of the diameter of the covered to that of the bare wire is the same for all sizes.

That this second assumption is incorrect is shown by the fact that the ratio for a No. 20 B. & S. gauge double silk-covered wire of the American Electrical Works is 1.12, while for a No. 40 wire it is 2.77.

In the course of the discussion we shall use the following symbols:

G, the galvanometer constant, field at center of coil per unit current.

I_G, galvanometer current.

D, deflection of instrument.

V, volume of the coil.

b, linear constant of the coil, $b = k\,(V)^{\frac{1}{3}}$.

R_G, the galvanometer resistance.

R, the resistance of the circuit external to the galvanometer.

C, the diameter of the covered wire.

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[1] Reprinted from the Physical Review, Vol. V, No. 5 (1897) pp. 300–305.

B, the diameter of the bare wire.

$y = C/B$.

w, the resistance per unit volume of the wire.

n, the number of turns per unit area.

E, E. M. F. of battery.

k, constants.

We shall assume an indefinitely short needle, and for the present retain the first assumption.

The usual demonstration is based on the equation,

$$G = k\sqrt{R_G}.$$

This equation requires correction. It is easily shown that

$$G = 4\pi nb\ (\phi.\, s),$$

where $(\phi.\, s)$ is a function the shape of the coil. As the same bobbin is to be used in all cases, we have

$$G = k_1 n = \frac{k_1}{C^2} = k_2 \frac{\sqrt{w}}{y} = k_3 \sqrt{\frac{R_G}{y^2}}.$$

To apply this to the typical circuit we have

$$I_G = \frac{E}{R + R_G}, \quad D = k_4\, I_G\, G = k_5\, \frac{E\sqrt{\frac{R_G}{y^2}}}{R + R_G}.$$

Differentiating and solving for a maximum, we have

$$R_G = \frac{R}{\frac{2}{y^2 \frac{d\left(\frac{R_G}{y^2}\right)}{dR_G}} - 1}$$

If y be constant, this reduces to

$$R_G = R,$$

the relation usually given.

This general formula was first given by Professor Silas W. Holman. In order to employ it the properties of the wire must be found by winding experimental coils.

The assumption of fixed dimensions will now be discarded, and attention given to the galvanometer constants of a family of similar instruments. For coils of rectangular cross section we have, referring to the diagram:

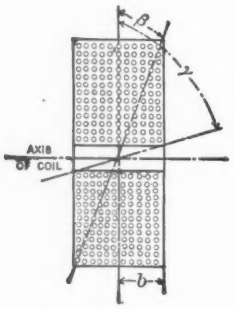

FIG. 1.

$$G = 4\pi nb \log_e \frac{\cot \frac{\beta}{2}}{\cot \frac{\gamma}{2}}$$

For coils of this shape,

$$\phi . s = \log_e \frac{\cot \frac{\beta}{2}}{\cot \frac{\gamma}{2}}.$$

For instruments of the same family, β and γ constant, we have:

$$G = k_6 nb = k_6 \frac{b}{yyB^2}$$

$$b = k_7 \left(\frac{R}{w}\right)^{\frac{1}{3}},$$

$$y = \frac{k_9}{B^2 w^{\frac{1}{3}}},$$

$$\therefore G = k_{10} \left(\frac{w^{\frac{1}{3}}}{y}\right) R_G^{\frac{1}{3}}.$$

This shows that the sensitiveness of similar galvanometers wound to various resistances with the same size of wire, is proportional to the cube root of the galvanometer resistance. Also for a family of instru-

ments of the same resistance the best size of wire will be that for which $\frac{w^{\frac{1}{2}}}{y}$ is a maximum. By winding experimental coils we obtain data for determining this function, a table of values of which is given below.

WIRE OF AMERICAN ELECTRICAL WORKS.

B. and S. Gauge No.	Single, Silk covered. $\frac{w^{\frac{1}{2}}}{y}$	Double, Silk covered. $\frac{w^{\frac{1}{2}}}{y}$	Ratio.
20	.94	.87	1.08
26	1.40	1.12	1.25
30	1.81	1.27	1.42
34	2.21	1.34	1.65
36	2.19	1.33	1.65
38	2.10	1.28	1.64
40	....	1.15	....

The results are plotted in Fig. 2.

The best size for both single and double-covered wire is seen to be No. 34. This result, of course, applies only to the particular make of wire examined.

We see that there may be two instruments of a family having the same resistance which will give equal deflections with the same current.

We are now in position to find the best galvanometer resistance. We have

$$D = k_{10}\left(\frac{w^{\frac{1}{2}}}{y}\right)\frac{R_G^{\frac{1}{2}}}{R+R_G}.$$

Considering for the moment that all the instruments are wound with the same size of wire, we have a maximum value of D when

$$R_G = R/2.$$

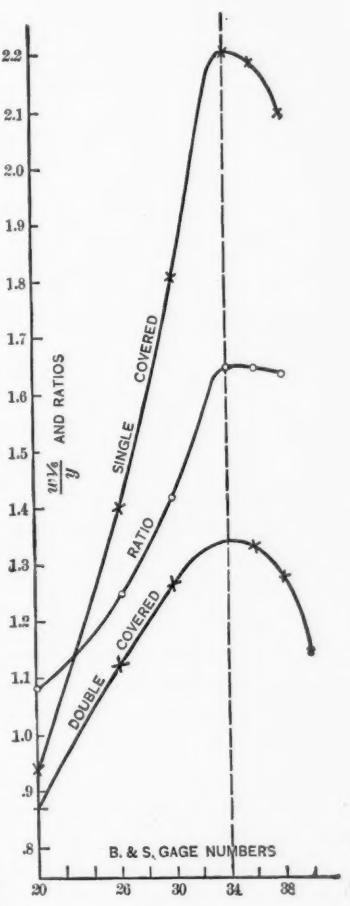

FIG. 2.

RELATIVE GALVANOMETER CONSTANTS FOR SIMILAR COILS WOUND TO THE SAME RESISTANCE WITH VARIOUS SIZES OF SILK-COVERED WIRE.

Therefore the best galvanometer of the family is one which is wound with a No. 34 wire to a resistance equal to one-half that of the remainder of the circuit.

We will now consider two special examples:

The coils of two-spool reflecting galvanometers very commonly have a volume of about eight cubic inches. Suppose the resistance external to the instrument to be 10ω and that double silk-covered wire is to be used, then by the ordinary rule the ideal galvanometer resistance is 10ω. In accordance with our first deduction No. 20 wire will give the best winding. R_G will then be 6ω.

$$D = k\, I_G\, G = k_1\, I_G\, nb\,;$$

$$D_{20} = k_1 \frac{E}{16.}\ 775.\ (8.)^{\frac{1}{2}}.$$

For the instrument wound with No. 34 wire we have $R_G = 5.\omega$, corresponding to a volume of coil of .026 cubic inches.

$$D_{34} = k_1 \frac{E}{15}.\ 7780.\ (.026)^{\frac{1}{2}};$$

$$\frac{D_{34}}{D_{26}} = 1.6 \text{ appox.}$$

The deflection of an instrument similar to the first, but designed in accordance with our suggestion, will be 60 per cent. greater than that of the instrument wound in accordance with what is called the solution for the best galvanometer resistance.

The coils of eight cubic inches would have a diameter of about 2.6″ and an axial breadth of about 1.5″. The approximate dimensions of the second coil would be diameter .4″, breadth .25″. The weight of wire in the first case would be 30. ounces, in the second, .032 ounces.

The results we have just obtained are in emphasis of the plea of Professor Boys for small instruments. In this connection we may observe that if we have two similar galvanometers of equal resistance, the first having a constant G_1, and wound with wire for which the ratio of the diameter covered to bare wire is y_1, while these quantities for the second instrument are G_2 and y_2, and if the linear dimensions of the first are N times those of the second, then,

$$\frac{G_2}{G_1} = \sqrt{N}\left(\frac{y_1}{y_2}\right).$$

The factor $\frac{y_1}{y_2}$ shows that there is a limit below which it is unprofitable to reduce the size of the instrument, this being the size for which a No. 34 wire is appropriate.

For galvanometers originally wound with wire finer than No. 34, the more sensitive instrument would be the larger.

We will now consider the case of a Wheatstone bridge where the resistances of the arms are small and nearly equal. Let them be of about one ohm each. Such an arrangement would be used in standardizing one-ohm coils, or in bolometric work.

The ordinary solution gives one ohm as the best galvanometer resistance. If the coil has a volume of 8 cubic inches, the winding should be of No. 16 wire making $R_G = .88\omega$. We will suppose the E. M. F. of the battery to be 1 volt, its resistance 1 ohm, and that the bridge is out of balance by $\frac{1}{1000}$ ohm; then with due regard to carrying capacity we have

$$I_G = \tfrac{1}{15000}. \text{ approx.}$$

$$D_{16} = k_1\ 325.\ (8)^{\frac{1}{3}}\ \tfrac{1}{15000}.$$

If wound as here indicated, we should have

$$R_G = .5\omega\ I_G = \tfrac{1}{12000}.$$

$$D_{34} = k_1\ 7780.\ (.0026)^{\frac{1}{3}}\ \tfrac{1}{12000}.$$

$$\frac{D_{34}}{D_{16}} = 2.04.$$

The deflection may be doubled by properly designing the galvanometer. This result is for double-covered wire. If single-covered be used, we should multiply by the ratio factor 1.65, giving

$$\frac{D_{34}}{D_{16}} = 3.36,$$

showing that by the use of a proper galvanometer wound with single-covered wire the sensitiveness of the bridge may be increased about 200 per cent.

The gain indicated in the examples is much greater with very low than with high resistance instruments, the former as usually wound departing more widely from the conditions here imposed.

Of course the numerical results indicate chiefly the order of magnitude of the gain, for it would be impossible to reduce the size of the instruments as much as is here indicated. Also we have not considered the magnetic system, or the fact that the space at the center of the coil must be large enough for free movement of the needle, and that turns in very close proximity to a finite needle produce less than the effect indicated by the strength of field at the center of the coil.

Our conclusions are, that if an existing arrangement of apparatus be taken, we can increase its sensitiveness by replacing the galvanometer by a similar instrument wound with wire of a particular size to a resistance equal to one-half of that of the remainder of the circuit. This best size of wire is that for which $\frac{w^3}{y}$ is a maximum.

For low resistance instruments the reduction in size renders magnetic shielding possible without undue clumsiness.

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July, 1897.

THE EXACT ESTIMATION OF TOTAL CARBOHYDRATES IN ACID HYDROLYZED STARCH PRODUCTS.[1]

By GEORGE W. ROLFE and W. A. FAXON.

Received June 11, 1897.

The determination of the exact amount of carbohydrates present in solutions of commercial glucose has always been conjectural, since the evaporation method, the only available means of estimation, has always caused in the residue an indeterminate amount of decomposition, usually attributed to oxidation or the destructive effect of high temperature. Since, however, in acid hydrolyzed starch products, it seems certain that the component carbohydrates preserve their individuality throughout the combinations which they may make with each other, at least so far as to have constant optical and chemical properties, as well as a constant influence on the specific gravity per unit weight of each present in solution, it is quite possible to determine the *proportional amount* of each constituent by the use of one arbitrary specific factor throughout the calculation. This has been explained in detail in several publications of O'Sullivan, Brown, Heron, Morris, and others. It is also well known that the factor used is that representing the increase in specific gravity caused by 1 gram of cane sugar in 100 cc. of solution.

It follows that if the specific gravity influences of the isolated carbohydrates were known it would be quite possible to predict the specific gravity factor of any hydrolyzed starch product. A year ago an attempt was made by one of us to predict these factors of the hydrolyzed starch products for all rotation between the limits of possible specific rotatory powers for the factor 386. A provisional curve was plotted from the following formula:

$$\Sigma = m\Sigma_m + g\Sigma_g + d\Sigma_d.$$

Σ being the specific gravity factor of the hydrolyzed starch product identified by its specific rotatory power; m, g, and d, the respective

[1] Reprinted from *Journal American Chemical Society*, Vol. XIX, No. 9.

percentages of maltose, dextrose, and dextrin present; and Σ_m, Σ_g, Σ_d, their corresponding specific gravity factors.

We considered this curve a provisional one, as we were obliged to approximate the factor for dextrin from the imperfect data of O'Sullivan, Salomon, and others, taking 0.00400 as the most probable value. The factors for dextrose and maltose were those of Salomon[1] for 10 per cent. solutions, 0.00381 and 0.00390, respectively. We found that the plotted values of the calculated factors, where the specific rotatory powers were expressed as abscissæ, formed a *straight line joining the plots corresponding to the factors taken for pure dextrin and dextrose* at the corresponding rotation of 195° and 53.5°.

Having defined approximate theoretical values we have sought to confirm them by actual determinations of the total solids present in a number of representative solutions prepared as previously described.[2]

Much ingenious apparatus[3] has been devised for overcoming the decomposition in drying already referred to. The principle of one class is the introduction of a presumably inert atmosphere, such as coal gas or hydrogen. Another class uses a vacuum, which mitigates at the same time oxidation and influence of high temperature.

Apparently, experience places so little confidence in the advantages of any of these multifarious appliances, at least in the case of sugars, that the ordinary method of drying at about 100° till the continual loss does not exceed a given rate per hour, is that usually recommended. We therefore at first dried 10 cc. each of solutions of hydrolyzed starch products on paper rolls at 105°–110° C.,[4] the rolls being placed in weighing beakers, and dried to practically constant weight in an oven kept at the given temperature. The results obtained were discordant, and in general lower than those of our provisional curve.

A second series of determinations were made by drying paper rolls, prepared in a similar way in a vacuum pan, the temperature being about 40°. In breaking the vacuum, air was passed through sulphuric acid and made to enter at the bottom of the pan to avoid the descent of moist vapors. Drying by this method was exceedingly tedious, and the values obtained are much lower than given by our

[1] J. prakt. Chem., 2, 28.

[2] This Journal, 18, 871–872.

[3] Wiley's Principles and Practice of Agricultural Analysis, Vol. III; see also recent bulletin by the U. S. Department of Agriculture.

[4] Rolfe and Defren: this Journal, 18, 872.

assumed curve, besides being discordant. They indicate the need of more heat in drying.

At this point in our work we received the important paper by Brown, Morris, and Millar,[1] giving the details of an elaborate investigation of the primary carbohydrates and of the products of diastase hydrolysis. In the latter the actual values were successfully predicted by a method similar to ours, but by a somewhat more exact formula, as it took into consideration variations in the factors due to those of concentration. These investigators used the drying apparatus designed by Lobray de Bryn and Von Laent[2] for the drying of maltose. This apparatus had worked so successfully for diastase converted solutions that we at once adopted a modification of it for our next essay. Several pieces of apparatus of the type described below (Figure 1) were

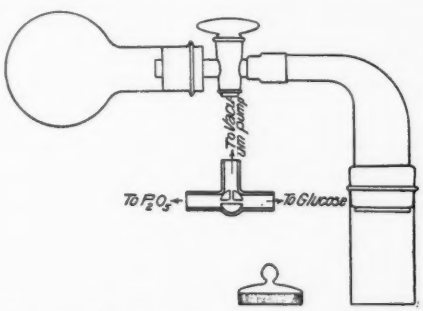

FIG. 1. — APPARATUS FOR DRYING SUGARS AND GLUCOSE SYRUPS.

improvised from the stock of material available. Our apparatus is arranged so that the greater bulk of the water can be first removed without coming in contact with the phosphorus pentoxide. This avoids previous evaporation on a water-bath. The tared weighing beaker containing the solution to be evaporated is slipped on the end of the adapter, an air-tight joint being made with "bill-tie" tubing. By the three-way stop-cock communication can be had with the vacuum pump, and with a 250 cc. flask containing phosphorus pentoxide, or either can be shut off.

The method of drying is as follows: The cock is opened to the pump only, and the air exhausted to 680–690 mm. The beaker is

[1] J. Chem. Soc., January, 1897.
[2] Rec. Trav. Chim., 1894, 13, 218.

lowered into an oil-bath and heated to about 100° till most of the water is evaporated. Communication is then made with the pentoxide flask, and the mass dried to constant weight at about 120°. For convenience, the vapors from the various pieces of apparatus were passed through a four-liter vacuum pan. This large receiver produced an almost instantaneous exhaustion when a stop-cock was opened. Complete drying usually required from eighteen to twenty-four hours. The slowness of our drying apparatus was possibly due to the contracted opening through the stop-cock, which may have prevented free circulation of vapors over the pentoxide. This drawback was the result of the necessary improvising of our apparatus from stock at hand.

The results obtained are tabulated in the following table and also

TABLE.

Number.	Time of drying. (Hours.)	Vol. of solution. (cc.)	$d_{15.5}$.	$\alpha_{D\,86}$.	Weight of residue.	Factor obtained.	Factor calculated.
1	18	10	1.02835	164.2	0.7104	0.003992	0.003980
2	18	10	1.03134	160.0	0.7833	0.003999	0.003974
3	24	10	1.03657	144.8	0.9223	0.003965	0.003954
4	18	10	1.03364	141.8	0.8509	0.003954	0.003950
5	24	10	1.04212	138.7	1.0644	0.003957	0.003946
6	18	10	1.03650	136.1	0.9222	0.003953	0.003942
8	18	10	1.03701	128.0	0.9376	0.003943	0.003931
9	24	10	1.03701	128.0	0.9417	0.003930	0.003931
11	18	10	1.03841	115.7	0.9781	0.003927	0.003918
12	18	10	1.03704	111.7	0.9454	0.003918	0.003911
13	18	10	1.03704	111.7	0.9465	0.003914	0.003911
15	24	10	1.03843	104.7	0.9827	0.003910	0.003901
16	18	10	1.03545	90.5	0.9127	0.003885	0.003883
17	18	10	1.03594	81.3	0.9282	0.003883	0.003871
18	18	10	1.03549	73.4	0.9162	0.003870	0.003860
19	18	10	1.03881	70.5	1.0081	0.003850	0.003856

(The omitted numbers are those of samples which were lost by breakage, or scorching due to loss of vacuum.)

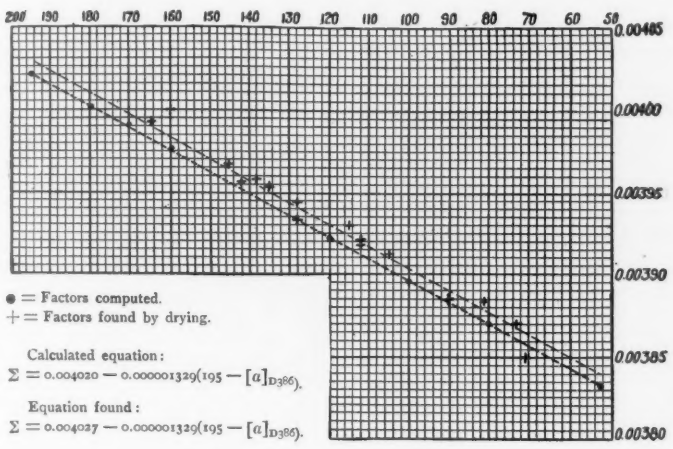

FIG. 2. — SPECIFIC GRAVITY FACTORS FOR APPROXIMATELY 10 PER CENT. SOLUTIONS OF HYDROLYZED STARCH PRODUCTS.

plotted in Figure 2. As will be seen, they form a straight line which is very slightly higher than the line calculated by using the revised carbohydrate values of Brown, Morris, and Millar. The variation is very slight, as the plot is drawn on a scale by which one division represents about 0.06 per cent. of the values obtained. The two equations obtained are more nearly concordant when we take into consideration that the average of the specific gravities of the samples is about 1.0360. This would raise the calculated value 0.000003 on the scale, or a little more than one-half of a division. We, therefore, have adopted as the most probable values what happens to be the mean. Our conclusion, then, is that within the concentrations expressed by the specific gravity factors, 1.035 and 1.045, we can calculate the absolute specific gravity influence of any acid hydrolyzed starch solution by the equation $\Sigma = 0.004023 - 0.000001329\ (195 - [\alpha]_D)$, when the specific rotatory power (obtained by the factor 0.00386) is known. These values within the limits of concentration given are correct to less than $\frac{2}{10}$ per cent. of their values. For commercial glucoses, the factor 0.00393, taken as a constant, is sufficiently exact for most determinations.

While this equation will now enable us to determine the exact amount of carbohydrate in solution when the specific gravity has

been previously corrected for the influence of other dissolved material, the simpler computation based on the factor 0.00386 will doubtless continue in use as more convenient for those calculations where proportion of carbohydrates is alone desired.

We have also under investigation the action of heat on commercial glucoses when samples are boiled down to candies, as well as the study of certain disturbing influences on the determination of cupric reducing powers of glucoses. The results are not yet complete enough for publication.